

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number  
**WO 2004/054524 A1**

(51) International Patent Classification<sup>7</sup>: **A61K 7/02**,  
7/027, 7/48

(21) International Application Number:  
PCT/EP2003/015024

(22) International Filing Date: 8 December 2003 (08.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
02/16039 17 December 2002 (17.12.2002) FR  
60/438,770 9 January 2003 (09.01.2003) US

(71) Applicant (for all designated States except US):  
L'ORÉAL [FR/FR]; 14, rue Royale, F-75008 Paris  
(FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BLIN, Xavier**  
[FR/FR]; 24, rue de Staël, F-75015 Paris (FR). **FERRARI,**  
**Véronique** [FR/FR]; 12, rue Saint Georges, F-94700  
Maisons-Alfort (FR).

(74) Agent: **BOULARD, Denis**; L'Oréal, D.I.P.L., 25-29, quai  
Aulagnier, F-92600 Asnières (FR).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR,  
CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,  
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,  
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,  
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU,  
SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,  
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: TRANSPARENT OR TRANSLUCENT CARE AND/OR MAKE-UP COSMETIC COMPOSITION STRUCTURED  
WITH SILICONE POLYMERS

(57) Abstract: Care and/or make-up cosmetic composition, which is transparent or translucent and/or capable of giving a transparent  
or translucent deposit, comprising a liquid fatty phase comprising at least one ester oil chosen from esters of monocarboxylic acids  
with monoalcohols and polyalcohols, structured with at least one structuring polymer (homopolymer or copolymer) having a weight-  
average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising at least one polyorganosiloxane  
group consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and at least two groups  
capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane,  
thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof, the polymer being solid at room temperature and  
soluble in the liquid fatty phase at a temperature of 25 to 250°C, and the liquid fatty phase and the structuring polymer forming a  
physiologically acceptable medium.

WO 2004/054524 A1

TRANSPARENT OR TRANSLUCENT CARE AND/OR MAKE-UP COSMETIC  
COMPOSITION STRUCTURED WITH SILICONE POLYMERS

Technical field

The present invention relates to a care  
5 and/or make-up cosmetic composition for the skin,  
including the scalp, and/or the lips of human beings,  
containing a liquid fatty phase comprising at least one  
ester silicone oil, gelled with a particular polymer,  
the said composition being transparent, translucent and  
10 provided in particular in the form of a cast make-up  
product, in particular as a make-up stick such as a  
lipstick, whose application leads to a deposit which is  
also transparent, translucent, nonsticky and transfer-  
free.

15 A care cosmetic composition is a composition  
which comprises at least one active compound for  
treating wrinkles, for moisturizing the skin and the  
lips, for protecting the skin, the lips and superficial  
body growths from ultraviolet rays, for treating acne  
20 and/or for acting as self-tanning agent.

The invention relates more particularly to  
cosmetic and dermatological compositions which are  
transparent and translucent, which may be coloured, and  
the deposits of which are also translucent and  
25 transparent, such as make-up products exhibiting non-  
stick and non-transfer properties.

Prior state of the art

In cosmetic or dermatological products, it is common to find a structured, namely gelled and/or rigidified, liquid fatty phase; this is in particular the case in solid compositions, balms and lipsticks, 5 eyeshadows, concealer products and foundations which have been cast. This structuring is obtained with the aid of waxes or fillers. Unfortunately, waxes and fillers have the drawback of rendering the composition opaque and tend to mattify the composition due to the 10 pressure of crystals, which is not always desirable in particular for a lipstick or an eyeshadow.

The expression liquid fatty phase is understood to mean, for the purposes of the application, a fatty phase which is liquid at room 15 temperature (25°C) and atmospheric pressure (760 mmHg), which is composed of one or more fatty substances which are liquid at room temperature, which are also called oils, which are compatible with each other and which 20 comprise at least one ester oil.

The expression structured liquid fatty phase is understood to mean a rigidified or gelled liquid fatty phase.

The expression rigidified liquid fatty phase 25 for the purposes of the application is understood to mean that this phase does not run under its own weight when a silicone polyamide is added thereto.

The expression gelled liquid fatty phase for the purposes of the application is understood to mean that the viscosity of this phase is increased because of the addition of silicone polyamide to this fatty phase.

The document EP-A-1 068 856 [1] describes solid cosmetic compositions, with no wax, containing a liquid fatty phase structured with a polymer, in which the fatty phase is mainly a non-silicone oil.

10 The document WO-A-01/97758 [2] describes cosmetic compositions based on polyamide resins comprising a gelling agent chosen from esters and amides of N-acylamino acids and mixtures thereof. The composition also comprises a solvent for the polyamide  
15 resin which may be chosen from unsaturated and saturated fatty alcohols, fatty and/or aromatic carboxylic acid esters, ethoxylated and/or propoxylated alcohols and acids, silicones, mineral oils and branched-chain hydrocarbons; preferably, fatty acid  
20 esters, fatty alcohols, mineral oils, branched hydrocarbons and mixtures thereof.

The fatty phases of cosmetic compositions often make use of silicone oils. Indeed, the use of fatty phases based on silicone oils makes it possible  
25 currently to obtain cosmetic compositions having a long staying power when the oils are only slightly volatile or are non-volatile, namely a good staying power in



particular of the colour over time (unchanging, unfading), and transfer-free compositions when the silicone oils are volatile, not forming a deposit on a support such as a glass, a cup, a fabric or a cigarette, placed in contact with the film of make-up.

Currently, the use of silicone oils in cosmetics is limited by the small number of molecules which can gel these media and thus give compositions which exist in solid form such as lipsticks or cast foundations for example.

The use of cosmetic compositions whose fatty phase is predominantly siliconized leads, in most cases, to problems of compatibility with the ingredients conventionally used in cosmetics.

In the documents WO-A-97/36573 [3], US-A-5 874 069 [4], US-A-5 919 441 [5], US-A-6 051 216 [6], WO-A-02/17870 [7], and WO-A-02/17871 [8], EP-A-1 177 784 [9], WO-A-99/06473 [13], and US-A-6 353 076 [14], which is a division of US-A-6 051 216 cosmetic compositions such as deodorant sticks or gels, comprising a silicone oily phase gelled with a polysiloxane- and polyamide-based wax, or with a polymer containing siloxane groups and groups capable of hydrogen interactions, have been prepared.

More particularly, the document WO-A-97 36573 [3] describes the combination of a fluid silicone solvent and thickening agents which are a wax

containing silicone groups, and a polyamide which may contain silicone groups.

The document US-A-5 874 069 [4] is close to the document WO-A-97 36573 [3], but it requires  
5 obtaining a solid system by passing from a clear and translucent system, and it gives details on the nature of the wax and its monomeric, in particular siloxane, units.

The document US-A-5 919 441 [5] describes a  
10 system containing a fluid with at least one silicone and a polymer with siloxane groups and H bond containing groups, the said polymer being a fluid at room temperature and being soluble in the fluid so as to obtain a clear and translucent solution.

15 The document US-A-6 051 216 [6] relates to the combination of a silicone polyamide with a fluid silicone and, optionally, an additional solvent.

In WO-A-02/17870 [7], it is envisaged to add to the composition another gelling agent, but the  
20 quantities added should be low, for example less than 0.5% in the case of hydroxystearic acid, in order to preserve the clarity of the product.

In WO-A-02/17871 [8], it is also envisaged to use a second gelling agent with the silicone polymer in  
25 a quantity representing 0.5 to 2% by weight of the composition, and a solvent system comprising a

non-silicone organic compound, a volatile silicone and optionally another silicone.

The document EP-A-1 177 784 [9] illustrates a deodorant composition comprising a liquid phase containing, for example, a volatile silicone and optionally a non-volatile silicone and/or a non-silicone hydrophobic organic liquid, structured with an organic compound with amido groups, with optionally one or more polymeric or non-polymeric secondary structuring agents in small proportions. Among the secondary structuring agents, this document mentions polymers having siloxane groups and groups exhibiting hydrogen interactions without giving examples or results on a composition using these polymers.

It should be stated that the documents [7], [8] and [9] relate to deodorants for which the problems of non-stickiness and non-transfer of the composition do not exist as in the case of the make-up cosmetic products described above.

It is evident in the light of the preceding text that the transparency is, in all cases, an extremely delicate property to obtain for a cosmetic composition, in particular a solid cast composition of lipstick, for example in stick form, regardless of the nature of the silicone oils or the like constituting the fatty phase. Indeed, the transparency or the translucent character cannot be obtained if waxes are

used for structuring the composition because, as indicated above, waxes have the disadvantage of making the composition opaque.

If it is sought to structure the composition, such as a stick, preferably without using waxes in order to avoid their opacifying effect, as is the case in the documents FR-A-2 817 740 [10] and FR-A-2 817 739 [11], other problems occur and the transparency is obtained at the detriment of other essential properties of the composition, such as the non-sticky character which is a property highly desired by the consumer.

It has not been possible until now to obtain a composition having, on the one hand, the attractive cosmetic appearance, which is represented by the transparency of the deposit and/or of the composition and, on the other hand, non-sticky and optionally transfer-free properties of the deposit formed from the said composition.

A need therefore exists for a cosmetic composition, in particular a solid cast composition, such as a lipstick, which is transparent or translucent and which furthermore gives a non-sticky deposit during its application. A need also exists for a cosmetic composition, in particular a coloured composition which is transparent or translucent and which makes it possible to obtain a deposit, which is in particular

coloured, transparent, non-sticky, but also does not transfer upon contact.

#### Disclosure of the invention

5           The aim of the invention is in particular to respond to the needs mentioned above.

          In other words, the aim of the invention is to provide a care and/or make-up composition for the skin and/or the lips, which makes it possible to  
10 overcome the disadvantages and to solve the problems mentioned above, in particular the aim of the invention is to provide a composition which is transparent or translucent and which also makes it possible to obtain a deposit which is non-sticky and does not transfer  
15 through contact.

          Surprisingly, the Applicant has found that the use of particular polymers, such as silicone polyamides, combined with a specific fatty phase comprising at least one ester-type oil, made it  
20 possible to achieve, inter alia, the above aims and to structure, in the absence of wax, the liquid fatty phases in the make-up or care compositions.

          In particular, it has been observed that the compositions containing this combination of a  
25 particular polymer and a specific ester oil were not only transparent and translucent, but also resulted in

non-sticky films or deposits with improved transfer-free properties.

The combination of these particular polymers with one or more ester oils present in the fatty phase makes it possible to obtain gels, in particular transparent or translucent, solid compositions having good mechanical strength and allowing a deposit in sufficient quantity, which is not sticky to the touch, which does not transfer upon contact and which is itself transparent or translucent.

The effects obtained by virtue of this combination of a particular polymer and a particular ester oil, in particular the combination of the non-transfer, of the absence of stickiness of the deposit and of the transparency or translucence of the composition and of the deposit, do not appear in the prior art documents.

The invention not only applies to make-up products for the lips such as lipsticks, lip pencils and lip glosses, but also to care products for the skin, including the scalp, and the lips, such as sun protection products in stick form for the skin, the face or the lips, or lip balms, to make-up products for the skin, both of the face and of the human body, such as foundations cast as a stick or in a dish, concealer products and temporary tattoo products, and to make-up products for the eyes such as eyeliners, in particular

in pencil form, and mascaras, in particular cakes for keratinous fibres (eyelashes, eyebrows, hair).

More precisely, the subject of the invention is a care and/or make-up cosmetic composition, which is  
5 transparent or translucent and/or capable of giving a transparent or translucent deposit, comprising :

- a liquid fatty phase comprising at least one ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at  
10 least one structuring polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group consisting  
15 of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and

- at least two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane,  
20 thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

- the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C, and

25 the liquid fatty phase and the structuring polymer forming a physiologically acceptable medium.

Cosmetic compositions comprising a liquid fatty phase comprising a specific ester oil, which are transparent or translucent, and whose structuring is additionally provided by a specific polymer, for example of the silicone polyamide type (PASI), are not described in the prior art.

Surprisingly, it has been found that the use, in the fatty phase of the composition of the invention, of a specific oil which is a so-called "ester" oil, which can be called "short ester", made it possible to obtain a transparent or translucent composition.

In addition, the compositions according to the invention give transparent or translucent deposits or films.

In other words, the cosmetic compositions of the invention have as a characteristic, on the one hand, the transparency or the translucence of the deposit which is obtained therefrom and, on the other hand, the translucent or transparent appearance of the composition before its application, "in the pot", "in the mass".

This property of transparency or of translucence "in the mass" means that a layer of the composition having a given thickness, allows a portion of visible light to pass through. If this portion of visible light is scattered, the composition will be defined as being a composition which is translucent in



the mass, and if, on the contrary, it is not scattered, then the composition will be defined as being a composition which is transparent in the mass.

The transparent or translucent property of the composition according to the invention is determined in the following manner: the test composition is cast into a 30 ml Volga pot, the composition is allowed to cool (for 24 h at room temperature) and a white sheet is placed on top, on which a cross about 2 mm thick is drawn with a black felt pen. If the cross is visible to the naked eye in daylight at an observation distance of 40 cm, the composition is transparent or translucent.

This transparent or translucent appearance is very satisfactory, in particular for the consumer, from an aesthetic point of view and may therefore be of great commercial interest.

The transparent or translucent character of a cosmetic composition, for example in stick form, and what is more, of the deposit obtained therefrom, is extremely difficult to predict.

It is absolutely not possible to know in advance which particular component and in which proportion, will make it possible to obtain the transparency or the translucence of the composition and, a fortiori of the deposit.

The formulation of transparent or translucent cosmetic compositions is therefore totally unpredictable and can in no case be deduced from pre-existing formulations or the properties, for example the optical properties, of the compounds entering into these compositions.

Nothing could have suggested that by choosing the specific "short" esters among the considerable number of oils capable of being incorporated into the fatty phase of a cosmetic composition, a transparent or translucent composition and a deposit of this translucent or transparent composition would surprisingly be obtained, given the random and highly unpredictable character of the transparency and the translucent character of a composition and of a deposit thereof.

It is surprising that the combination of this specific ester with a specific structuring polymer, for example of the PAsi type, leads to a composition which, while being transparent or translucent and giving a transparent or translucent deposit, also makes it possible to obtain a deposit which is "transfer-free" upon contact and which is not sticky.

Now, it has been found that only the specific esters according to the invention made it possible, among all the oils capable of being used in the cosmetic compositions, to obtain surprisingly, with the

particular structuring polymers described above, and in the absence or in the presence of a small quantity of waxes, structured systems, such as gels or sticks exhibiting transparency/translucence, and formulations which are not sticky ("non-sticky") and which do not transfer upon contact.

The invention results from the double selection, from a very large number of oils and of structuring polymers respectively, of a specific oil and of a specific polymer whose combination surprisingly leads to a system which exhibits the combination of advantageous properties according to the invention.

In connection with the preceding text, the transfer-resistance of a cosmetic composition may be estimated by a transfer-resistance test which is well established in the technical field, such as the application of the made-up area on the skin or the lips (the so-called "kiss" test). The same applies to the non-sticky test (see Example 4).

The transparent or translucent composition of the invention may be provided in the form of a paste, a solid or a more or less viscous cream. It may be a simple or multiple, in particular an oil-in-water or a water-in-oil, a water-in-oil-in water or an oil-in-water-in oil, emulsion, or a rigid or soft gel having an oily continuous phase. The simple or multiple

emulsion may comprise an aqueous or oily continuous phase optionally containing dispersed lipid vesicles.

In particular, it is provided in a form cast as a stick or in a dish and more especially in the form of an  
5 oily, in particular anhydrous, rigid gel and in particular of an anhydrous stick. More especially, it is provided in the form of a translucent or transparent rigid gel and preferably, if the composition contains pigments or dyes, a slightly coloured rigid gel, the  
10 liquid fatty phase forming the continuous phase. An anhydrous composition will comprise less than 10% by weight of water, for example less than 5% by weight.

The structuring of the liquid fatty phase can be modulated according to the nature of the structuring  
15 polymer and the ester oil used; this structuring may be such that a rigid structure is obtained in the form of a baton or a stick, having good mechanical strength, which is transparent or translucent. When they are coloured, these batons make it possible, after  
20 application, to obtain a deposit which is transparent, translucent, non-transfer and non-sticky.

The composition may contain one or more structuring polymers, as defined above, and one or more ester oils.

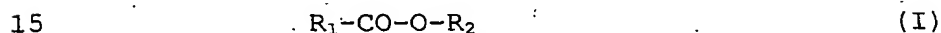
Advantageously, the composition of the invention is a composition for the lips and even better a lipstick composition in particular in stick form.

5 Liquid fatty phase

The liquid fatty phase of the composition of the invention comprises one or more oils.

According to the invention, at least one of these oils is an oil called "ester oil" which is chosen  
10 from esters of monocarboxylic acids with monoalcohols and polyalcohols.

Advantageously, the said ester corresponds to the following formula (I):



where  $R_1$  represents a linear or branched alkyl radical of 1 to 40 carbon atoms, preferably of 7 to 19 carbon atoms, optionally comprising one or more  
20 ethylenic double bonds, and optionally substituted,

$R_2$  represents a linear or branched alkyl radical of 1 to 40 carbon atoms, preferably of 3 to 30 carbon atoms and even better of 3 to 20 carbon atoms, optionally comprising one or more ethylenic double  
25 bonds, and optionally substituted.

The expression "optionally substituted" is understood to mean that  $R_1$  and/or  $R_2$  may carry one or more substituents chosen for example from groups comprising one or more heteroatoms chosen from O, N and S, such as amino, amine, alkoxy, hydroxyl.

Preferably, the total number of carbon atoms of  $R_1 + R_2$  is  $\geq 9$ .

The ester used according to the invention may be designated under the name of "short" ester.

$R_1$  may represent the residue of a preferably higher, linear or, preferably branched fatty acid comprising from 1 to 40 and even better from 7 to 19 carbon atoms and  $R_2$  may represent a linear or preferably branched hydrocarbon chain containing from 1 to 40, preferably from 3 to 30 and even better from 3 to 20 (19 to 28, 8 to 27, 7 to 26 C) carbon atoms. Again, preferably the number of carbon atoms of  $R_1 + R_2 \geq 9$ .

Examples of  $R_1$  groups are those derived from fatty acids chosen from the group consisting of acetic, propionic, butyric, caproic, caprylic, pelargonic, capric, undecanoic, lauric, myristic, palmitic, stearic, isostearic, arachidic, behenic, oleic, linolenic, linoleic, oleostearic, arachidonic and erucic acids, and mixtures thereof.

Examples of esters which can be used in the fatty phases of the compositions of the invention are for example purcellin oil (cetostearyl octanoate),

isononyl isononanoate, isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate, isostearyl isostearate, and heptanoates, octanoates, decanoates or ricinoleates of alcohols or polyalcohols, for example of fatty alcohols.

Advantageously, the esters are chosen from the compounds of formula (I) above, in which  $R_1$  represents an unsubstituted linear or branched alkyl group, optionally comprising one or more ethylenic double bonds, from 1 to 40 carbon atoms, preferably from 7 to 19 carbon atoms, and  $R_2$  represents an unsubstituted linear or branched alkyl group, optionally comprising one or more ethylenic double bonds, from 1 to 40 carbon atoms, preferably from 3 to 30 carbon atoms, and even better from 3 to 20 carbon atoms.

Preferably,  $R_1$  is an unsubstituted branched alkyl group of 4 to 14 carbon atoms, preferably of 8 to 10 carbon atoms, and  $R_2$  is an unsubstituted branched alkyl group of 5 to 15 carbon atoms, preferably of 9 to 11 carbon atoms. Preferably, in formula (I),  $R_1$ -CO- and  $R_2$  have the same number of carbon atoms and are derived from the same radical, preferably an unsubstituted branched alkyl, for example isononyl, that is to say that advantageously the ester oil molecule is symmetrical.

The ester oil will be preferably chosen from the following compounds:

- isononyl isononanoate,
- cetostearyl octanoate,
- 5 - isopropyl myristate,
- 2-ethylhexyl palmitate,
- 2-octyldodecyl stearate,
- 2-octyldodecyl erucate,
- isostearyl isostearate.

10

The ester which is preferred amongst all is isononyl isononanoate which makes it possible to obtain at best compositions having excellent transparency or translucence combined with excellent properties of non-transfer and absence of stickiness.

15

Advantageously, the fatty phase comprises from 0.5 to 100% by weight of oil or of ester oils, preferably from 1 to 80% by weight, still more preferably from 2 to 50% by weight, even better from 20 to 40% by weight.

20

In these percentage ranges, the surprising effects of the invention, namely essentially the combination of transparency/translucence, non-transfer, and non-stickiness are exhibited with the greatest magnitude.

25

Preferably, the fatty phase comprises 100% by weight of the ester oil(s), that is to say that the



fatty phase contains, as oils, only ester oils as described above, excluding any other oil.

More preferably still, the fatty phase comprises only one ester oil (and not a mixture) which is preferably isononyl isononanoate, this single ester oil being present in the above percentages, and preferably in an amount of 100% by weight.

The liquid fatty phase of the composition according to the invention comprises at least one oil generally chosen from hydrocarbon, silicone and fluorinated oils.

An oil is a nonaqueous compound which is immiscible with water.

The liquid fatty phase may comprise at least one volatile oil.

For the purposes of the invention, a volatile oil has a flash point preferably of 35 to 135°C (measured according to the method) or no flash point. The flash point is the temperature at which the vapours emitted by a fuel ignite upon contact with a flame, a spark or a heat source.

Volatile oils have advantageously at room temperature (25°C) and atmospheric pressure (760 mmHg) a vapour pressure ranging from 0.01 mm to 300 mmHg (1.33 Pa to 40 000 Pa) and even better ranging from 0.05 to 190 mmHg (6.65 Pa to 25 330 Pa).

According to the invention, the volatile oil may be chosen from linear, branched or cyclic silicone oils having a flash point equal to or greater than 40°C and/or a viscosity of less than 8 cSt, such as linear, 5 branched or cyclic polydimethylsiloxanes (PDMS) having from 3 to 7 silicon atoms.

By way of examples of such volatile oils, there may be mentioned the compounds given in Table 1 below.

10 The composition may contain a non-volatile silicone oil.

The silicone oils of the invention have a viscosity which is advantageously chosen from the ranging going from 5 to 800 000 cSt at 25°C, preferably 15 from 10 to 500 000 cSt, and even better from 10 to 5 000 cSt.

The non-volatile silicone oils may be polydimethylsiloxanes, polyalkylmethylsiloxanes, dimethicone copolyols, alkylmethicone copolyols, 20 cetyldimethicone, silicones with alkylglyceryl ether groups, silicones with side amine groups and dilauroyltrimethylol propane siloxysilicate. The alkyl groups of these oils have in particular from 2 to 24 carbon atoms.

25 The non-volatile silicone oils may be polydimethylsiloxanes, polyalkylmethylsiloxanes, dimethicone copolyols, alkylmethicone copolyols,

cetyldimethicone, silicones with alkylglyceryl ether groups, silicones with side amine groups and dilauroyltrimethylol propane siloxysilicate. The alkyl groups of these oils have in particular from 2 to 24 carbon atoms.

The non-volatile silicone oils which can be used in the invention may be in particular linear, non-volatile polydimethylsiloxanes (PDMS) which are liquid at room temperature; polydimethylsiloxanes containing alkyl, alkoxy or phenyl groups, which are pendent and/or at the silicone chain end, groups each having from 2 to 24 carbon atoms; phenylated silicones such as phenyltrimethicones, phenyldimethicones, phenyltrimethylsiloxo diphenylsiloxanes, diphenyldimethicones, diphenylmethyldiphenyltrisiloxanes, 2-phenylethyl trimethylsiloxysilicates, fluorinated silicones with one or more group(s) that is (are) pendent or at the chain end having from 1 to 12 carbon atoms of which all or some of the hydrogen atoms are substituted with fluorine atoms, dimethiconols and mixtures thereof.

Table 1

Compound	Flash point (°C)	Viscosity (cSt)
Octyltrimethicone	93	1.2
Hexyltrimethicone	79	1.2
Decamethylcyclopentasiloxane (cyclopentasiloxane or D5)	72	4.2
Octamethylcyclotetrasiloxane (cyclotetradimethylsiloxane or D4)	55	2.5
Dodecamethylcyclohexasiloxane (D6)	93	7
Decamethyltetrasiloxane (L4)	63	1.7
KF 96 A from Shin Etsu	94	6
PDMS (polydimethylsiloxane) DC 200 (1.5 cSt) from Dow Corning	56	1.5
PDMS DC 200 (2 cSt) from Dow Corning	87	2
PDMS DC 200 (5 cSt)	134	5

from Dow Corning		
PDMS DC 200 (3 cSt)	102	3
from Dow Corning		

In other words, the volatile silicone oil(s) may be chosen, for example, from the group consisting of the compounds of Table 1, heptamethyloctyltrisiloxane, dodecamethylpentasiloxane and mixtures thereof.

The volatile silicone oil may also be chosen from the group comprising fluorinated silicone oils such as silicones with alkyl and perfluoroalkyl groups, silicones with oxyethylenated/oxypropylenated (EO/PP) side groups and with perfluorinated groups, silicones with perfluorinated side groups and with glycerolated side groups, perfluoroalkylmethylphenylsiloxanes, these oils having a vapour pressure greater than or equal to 0.02 mmHg.

The volatile non-silicone oils may be chosen from the group comprising hydrocarbon oils and volatile esters and ethers such as volatile hydrocarbons such as isododecane and isohexadecane, C<sub>8</sub>-C<sub>16</sub> isoparaffins, isohexyl or isodecyl neopentanoates.

The volatile oil may also be chosen from fluorinated oils such as perfluoropolyethers, perfluoroalkanes such as perfluorodecalin, perfluorodamantanes, esters (monoesters, diesters and

triesters) of perfluoroalkyl phosphates and fluorinated ester oils.

By way of example of volatile non-silicone oils which can be used in the invention, there may be mentioned the compounds of Table 2 which follows.

Table 2

Compound	Flash point (°C)
Isododecane	43
Isohexadecane	102
Isodecyl neopentanoate	118
Propylene glycol n-butyl ether	60
Ethyl 3-ethoxypropionate	58
Propylene glycol methyl ether acetate*	46
Isopar L (C <sub>11</sub> -C <sub>13</sub> isoparaffin)	62
Isopar H (C <sub>11</sub> -C <sub>12</sub> isoparaffin)	56

The liquid fatty phase advantageously contains at least 1%, and even better at least 5%, for example from 10 to 90%, by weight of silicone oil(s) advantageously having a viscosity of less than 1 000 cSt and even better of less than 100 cSt because the silicone polymers used in the invention are more soluble in silicone oils of low viscosity.

When the fatty phase comprises a volatile oil, it advantageously represents from 3 to 89.4%, and even better from 5 to 60%, for example from 5 to 20% of the total weight of the composition.

5           The liquid fatty phase may also contain other non-silicone oils, for example polar oils such as:

    - hydrocarbonaceous vegetable oils with a high content of triglycerides consisting of esters of fatty acids and of glycerol in which the fatty acids may have  
10 varied chain lengths, it being possible for the latter to be linear or branched, saturated or unsaturated; these oils are in particular wheat germ, maize, sunflower, karite, castor, sweet almond, macadamia, apricot, soybean, rapeseed, cottonseed, lucerne, poppy  
15 seed, pumpkin seed, sesame, gourd, avocado, hazelnut, grapeseed or blackcurrant seed, evening primrose, millet, barley, quinoa, olive, rye, safflower, candlenut, passion flower and rose musk oils; or triglycerides of caprylic/capric acids such as those  
20 sold by the company Stearines Dubois or those sold under the names Miglyol 810, 812 and 818 by the company Dynamit Nobel;

    - synthetic esters having from 10 to 40 carbon atoms;

25           -  $C_8$  to  $C_{26}$  fatty alcohols such as oleyl alcohol and octyldodecanol;

- fatty acids such as oleic, linoleic or linolenic acid; and

- mixtures thereof.

The liquid fatty phase may also contain  
5 apolar oils such as linear or branched hydrocarbons or fluorocarbons of synthetic or mineral origin, which are volatile or not, such as volatile oils of paraffin (such as isoparaffins, isododecane) or non-volatile oils of paraffin and its derivatives, petroleum jelly,  
10 polydecenes, hydrogenated polyisobutene such as parleam, squalane, and mixtures thereof.

Thus, the invention may be used for example with the following different fatty phases:

1) a fatty phase consisting solely of a mixture of  
15 ester oils;

2) a fatty phase consisting solely of a single ester oil;

3) a fatty phase consisting of a mixture of oils comprising at least one ester oil and at least one  
20 volatile silicone oil;

4) a fatty consisting of a mixture of oils comprising at least one ester oil and at least one non-silicone volatile oil;

5) a fatty phase consisting a mixture of oils  
25 comprising at least one ester oil, at least one non-silicone volatile oil and optionally one volatile silicone oil;



6) a fatty phase consisting of a mixture of oils comprising at least one ester oil, one non-volatile, non-silicone oil and optionally at least one volatile non-silicone oil; and

5 in cases 3), 4) and 5), the mixture may also comprise a non-volatile non-silicone oil.

Generally, the liquid fatty phase represents from 5 to 95% of the total weight of the composition and even better from 20 to 75%.

10 According to the invention, the composition comprises, in addition, solid particles chosen from fillers and pigments (including pearlescent pigments), and mixtures thereof, in a quantity such that the composition remains transparent or translucent.

15 The expression pigments is understood to mean any solid particle insoluble in the composition which serves to give and/or modify a colour and/or an iridescent appearance.

The pigments may be white or coloured,  
20 inorganic and/or organic, coated or not. Inorganic pigments may be chosen, for example, from zinc oxides, iron oxides, titanium oxides and mixtures thereof. There thus may be mentioned, among the inorganic pigments, titanium or zinc dioxide, optionally surface-  
25 treated, zirconium or cerium oxides, and iron or chromium oxides, manganese violet, ultramarine blue, chromium hydrate and ferric blue. Among the organic

pigments, there may be mentioned carbon black, pigments of the D & C type, and lacquers based on carmine, barium, strontium, calcium or aluminium. The pigments may represent from 0.1 to 30% of the total weight of the composition, preferably from 2 to 15%, if they are present.

#### Structuring silicone polymer

The structuring polymer(s) of the composition are solid at room temperature (25°C) and atmospheric pressure (760 mmHg) and are soluble in the liquid fatty phase at a temperature of 25 to 250°C.

The expression polymer is understood to mean, for the purpose of the invention, a compound having at least 2 repeating moieties, preferably at least 3 repeating moieties and even better 10 repeating moieties.

In the composition of the invention, the structuring silicone polymer of the gelling system generally represents from 0.5 to 80%, preferably from 2 to 60% and even better from 5 to 40% of the total weight of the composition.

Moreover, the structuring polymer/total oil(s) mass ratio of the composition is preferably from 0.01 to 0.8, more preferably from 0.05 to 0.5 and better still from 0.1 to 0.5.

The structuring polymer/ester oil mass ratio is generally from 0.01 to 10, preferably from 0.05 to 5 and more preferably from 0.1 to 2.

The polymers used as structuring agents in the composition of the invention are polymers of the polyorganosiloxane type such as those described in the documents US-A-5 874 069 [4], US-A-5,919,441 [5], US-A-6,051,216 [6] and US-A-5,981,680 [12].

According to the invention, the polymers used as structuring agent may belong to the following two families:

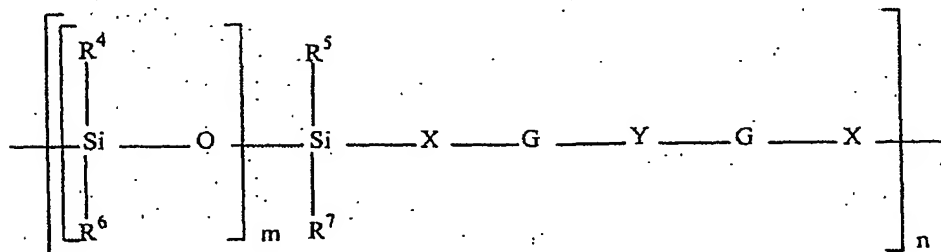
1) polyorganosiloxanes comprising at least two groups capable of establishing hydrogen interactions, these two groups being situated in the polymer chain; and/or

2) polyorganosiloxanes comprising at least two groups capable of establishing hydrogen interactions, these two groups being situated on the grafts or branches.

The polymers to which the invention applies are solids which may be solubilized beforehand in a solvent with hydrogen interactions, capable of breaking the hydrogen interactions of the polymers, such as C<sub>2</sub> to C<sub>8</sub> lower alcohols and in particular ethanol, n-propanol or isopropanol, before being brought into contact with the silicone oils according to the invention.

The polymers comprising two groups capable of establishing hydrogen interactions in the polymer chain may be polymers comprising at least one moiety corresponding to the formula:

5



(II)

in which:

1)  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$ , which may be identical or  
10 different, represent a group chosen from:

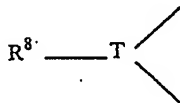
- linear, branched or cyclic, saturated or unsaturated,  $\text{C}_1$  to  $\text{C}_{40}$  hydrocarbon-based groups, possibly containing in their chain one or more oxygen, sulphur and/or nitrogen atoms, and possibly being  
15 partially or totally substituted with fluorine atoms,
- $\text{C}_6$  to  $\text{C}_{10}$  aryl groups, optionally substituted with one or more  $\text{C}_1$  to  $\text{C}_4$  alkyl groups,
- polyorganosiloxane chains possibly containing one or more oxygen, sulphur and/or nitrogen atoms;

20 2) the groups X, which may be identical or different, represent a linear or branched  $\text{C}_1$  to  $\text{C}_{30}$

alkylenediyl group, possibly containing in its chain one or more oxygen and/or nitrogen atoms;

3) Y is a saturated or unsaturated, C<sub>1</sub> to C<sub>50</sub> linear or branched divalent alkylene, arylene, cycloalkylene, alkylarylene or arylalkylene group, possibly comprising one or more oxygen, sulphur and/or nitrogen atoms, and/or bearing as substituent one of the following atoms or groups of atoms: fluorine, hydroxyl, C<sub>3</sub> to C<sub>8</sub> cycloalkyl, C<sub>1</sub> to C<sub>40</sub> alkyl, C<sub>5</sub> to C<sub>10</sub> aryl, phenyl optionally substituted with 1 to 3 C<sub>1</sub> to C<sub>3</sub> alkyl groups, C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl and C<sub>1</sub> to C<sub>6</sub> aminoalkyl, or

4) Y represents a group corresponding to the formula:



in which

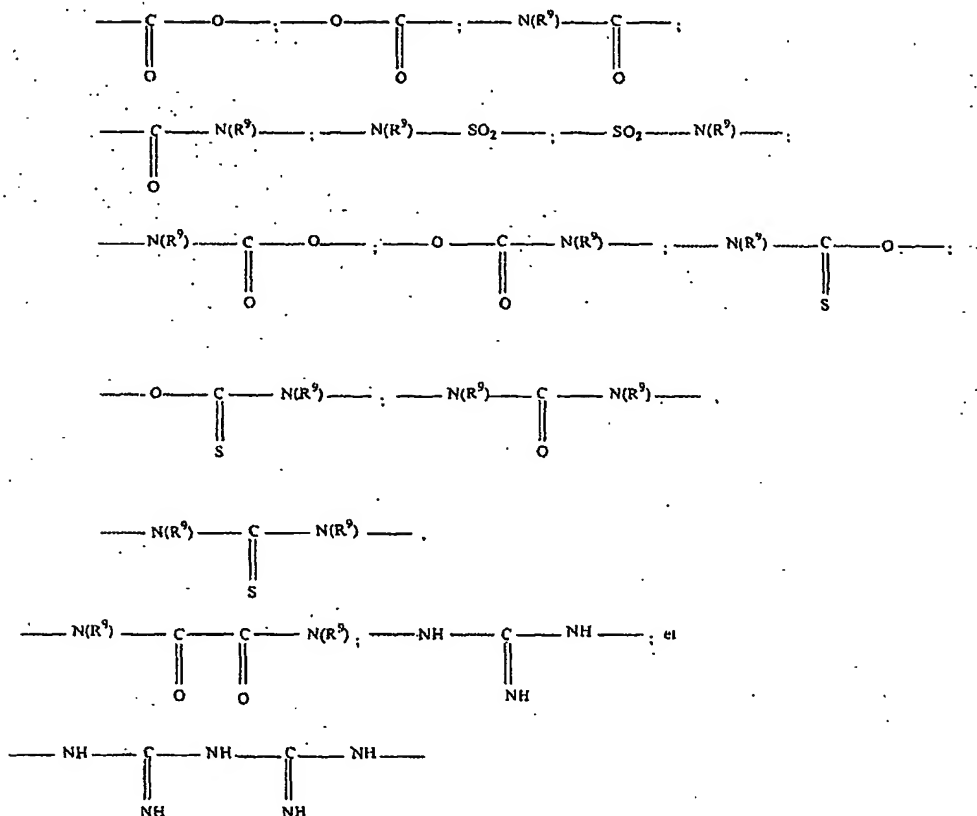
- T represents a linear or branched, saturated or unsaturated, C<sub>3</sub> to C<sub>24</sub> trivalent or tetravalent hydrocarbon-based group optionally substituted with a polyorganosiloxane chain, and possibly containing one or more atoms chosen from O, N and S, or T represents a trivalent atom chosen from N, P and Al, and

- R<sup>8</sup> represents a linear or branched C<sub>1</sub> to C<sub>50</sub> alkyl group or a polyorganosiloxane chain, possibly comprising one or more ester, amide, urethane, thiocarbamate, urea, thiourea and/or sulphonamide

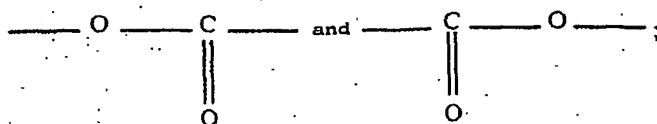
groups, which may possibly be linked to another chain of the polymer;

5) the groups G, which may be identical or different, represent divalent groups chosen from:

5.



in which R<sup>9</sup> represents a hydrogen atom or a linear or branched C<sub>1</sub> to C<sub>20</sub> alkyl group, on condition that at least 50% of the groups R<sup>9</sup> of the polymer represent a hydrogen atom and that at least two of the groups G of the polymer are a group other than:



- 6) n is an integer ranging from 2 to 500 and preferably from 2 to 200, and m is an integer ranging from 1 to 1 000, preferably from 1 to 700 and better.
- 5 still from 6 to 200.

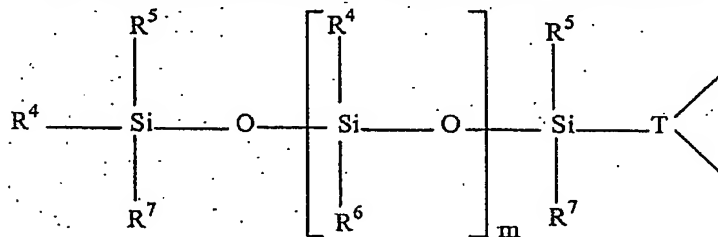
According to the invention, 80% of the groups  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  of the polymer are preferably chosen from methyl, ethyl, phenyl and 3,3,3-trifluoropropyl groups.

- 10 According to the invention, Y can represent various divalent groups, furthermore optionally comprising one or two free valencies to establish bonds with other moieties of the polymer or copolymer. Preferably, Y represents a group chosen from:

- 15 a) linear  $C_1$  to  $C_{20}$  and preferably  $C_1$  to  $C_{10}$  alkylene groups,
- b)  $C_{30}$  to  $C_{56}$  branched alkylene groups possibly comprising rings and unconjugated unsaturations,
- c)  $C_5$ - $C_6$  cycloalkylene groups,
- 20 d) phenylene groups optionally substituted with one or more  $C_1$  to  $C_{40}$  alkyl groups,
- e)  $C_1$  to  $C_{20}$  alkylene groups comprising from 1 to 5 amide groups,

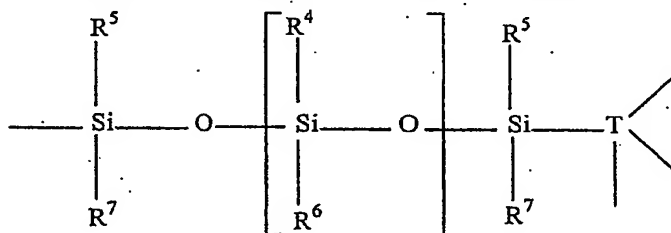
f)  $C_1$  to  $C_{20}$  alkylene groups comprising one or more substituents chosen from hydroxyl,  $C_3$  to  $C_8$  cycloalkane,  $C_1$  to  $C_3$  hydroxyalkyl and  $C_1$  to  $C_6$  alkylamine groups,

5 g) polyorganosiloxane chains of formula:



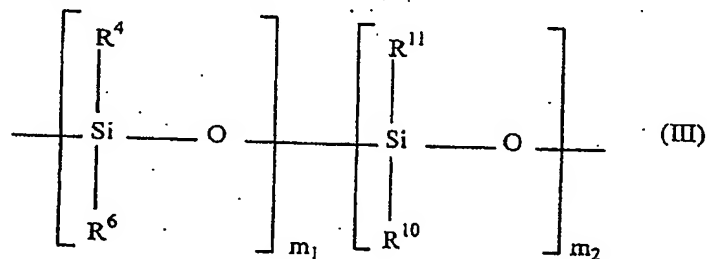
in which  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ , T and m are as defined above,  
and

h) polyorganosiloxane chains of formula:



10

The polyorganosiloxanes of the second family may be polymers comprising at least one moiety corresponding to formula (III):



15 in which



- $R^4$  and  $R^6$ , which may be identical or different, are as defined above for formula (II),
- $R^{10}$  represents a group as defined above for  $R^4$  and  $R^6$ , or represents the group of formula  $-X-G-R^{12}$  in which X and G are as defined above for formula (II) and  $R^{12}$  represents a hydrogen atom or a linear, branched or cyclic, saturated or unsaturated,  $C_1$  to  $C_{50}$  hydrocarbon-based group optionally comprising in its chain one or more atoms chosen from O, S and N, optionally substituted with one or more fluorine atoms and/or one or more hydroxyl groups, or a phenyl group optionally substituted with one or more  $C_1$  to  $C_4$  alkyl groups,
- $R^{11}$  represents the group of formula  $-X-G-R^{12}$  in which X, G and  $R^{12}$  are as defined above,
- $m_1$  is an integer ranging from 1 to 998, and
- $m_2$  is an integer ranging from 2 to 500.

According to the invention, the polymer used as structuring agent may be a homopolymer, that is to say a polymer comprising several identical moieties, in particular moieties of formula (II) or of formula (III).

According to the invention, it is also possible to use a polymer consisting of a copolymer comprising several different moieties of formula (II), that is to say a polymer in which at least one of the groups  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ , X, G, Y, m and n is different in one of the moieties. The copolymer may also be formed

from several moieties of formula (III), in which at least one of the groups  $R^4$ ,  $R^6$ ,  $R^{10}$ ,  $R^{11}$ ,  $m_1$  and  $m_2$  is different in at least one of the moieties.

It is also possible to use a copolymer comprising at least one moiety of formula (II) and at least one moiety of formula (III), the moieties of formula (II) and the moieties of formula (III) possibly being identical to or different from each other.

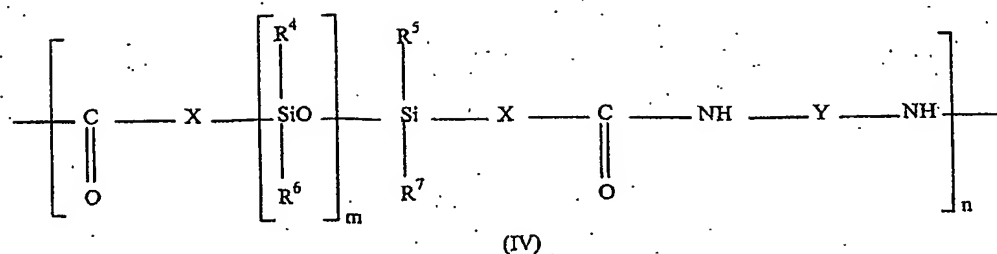
According to one variant of the invention, it is also possible to use a copolymer furthermore comprising at least one hydrocarbon-based moiety comprising two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof.

These copolymers may be block copolymers or graft copolymers.

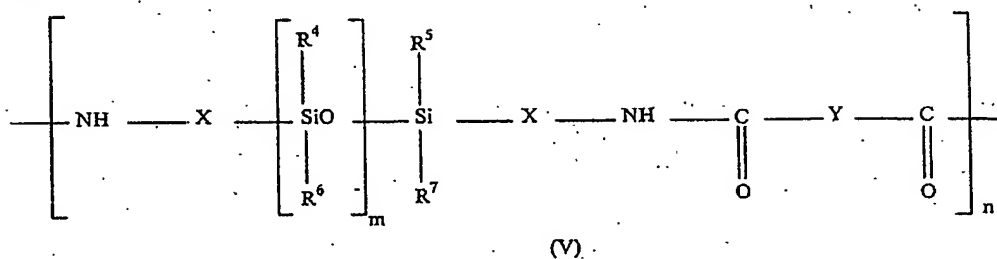
According to a first embodiment of the invention, the groups capable of establishing hydrogen interactions are amide groups of formulae  $-C(O)NH-$  and  $-HN-C(O)-$ .

In this case, the structuring agent may be a polymer comprising at least one moiety of formula (IV) or (V):

38



or

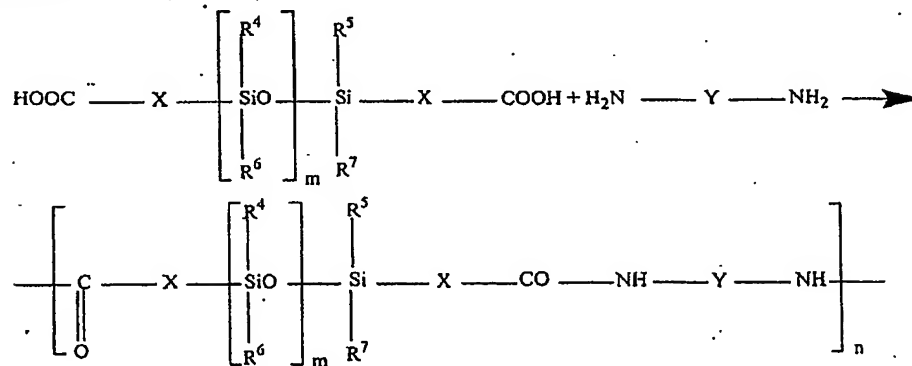


in which  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{X}$ ,  $\text{Y}$ ,  $m$  and  $n$  are as defined  
 5 above.

Such a moiety may be obtained:

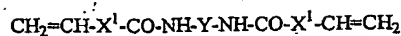
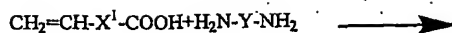
- either by a condensation reaction between a  
 silicone containing  $\alpha, \omega$ -carboxylic acid ends and one or  
 more diamines, according to the following reaction

10 scheme:

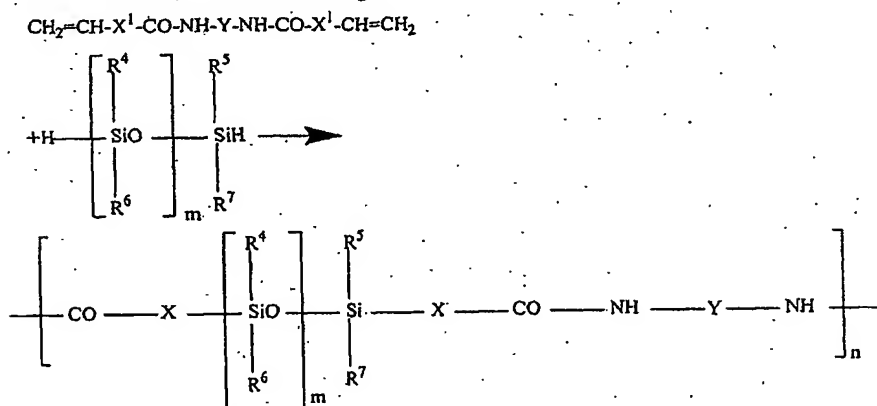


- or by reaction of two molecules of  $\alpha$ -unsaturated  
 carboxylic acid with a diamine according to the  
 following reaction scheme:

39.



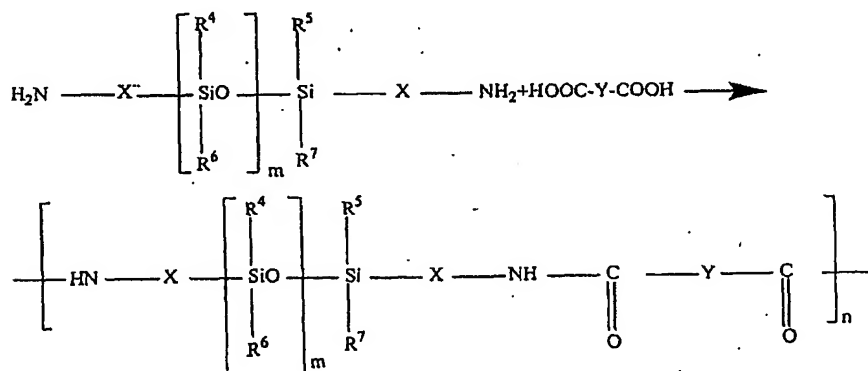
followed by the addition of a siloxane to the ethylenic unsaturations, according to the following scheme:



5 in which  $\text{X}^1-(\text{CH}_2)_2-$  corresponds to X defined above and Y,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and m are as defined above;

- or by reaction of a silicone containing  $\alpha, \omega$ - $\text{NH}_2$  ends and a diacid of formula  $\text{HOOC}-\text{Y}-\text{COOH}$  according to the following reaction scheme:

10



In these polyamides of formula (IV) or (V), m is preferably in the range from 1 to 700, more preferably from 15 to 500 and better still from 10 to 100, and n is in particular in the range from 1 to 500, preferably from 1 to 100 and better still from 4 to 25,

X is preferably a linear or branched alkylene chain containing from 1 to 30 carbon atoms and in particular 3 to 10 carbon atoms, and

- Y is preferably an alkylene chain that is linear or branched or that possibly comprises rings and/or unsaturations, containing from 1 to 40 carbon atoms, in particular from 1 to 20 carbon atoms and better still from 2 to 6 carbon atoms, in particular 6 carbon atoms.

In formulae (IV) and (V), the alkylene group representing X or Y can optionally contain in its alkylene portion at least one of the following elements:

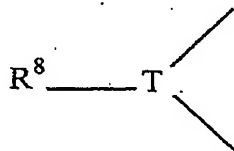
- 1) 1 to 5 amide, urea, urethane or carbamate groups,
- 2) a C<sub>5</sub> or C<sub>6</sub> cycloalkyl group, and
- 3) a phenylene group optionally substituted with 1 to 3 identical or different C<sub>1</sub> to C<sub>3</sub> alkyl groups.

In formulae (IV) and (V), the alkylene groups may also be substituted with at least one element chosen from the group consisting of:

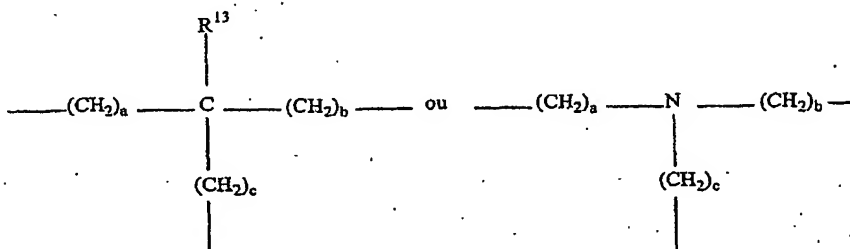
- a hydroxyl group,
- a C<sub>3</sub> to C<sub>8</sub> cycloalkyl group,

- one to three C<sub>1</sub> to C<sub>40</sub> alkyl groups,
- a phenyl group optionally substituted with one to three C<sub>1</sub> to C<sub>3</sub> alkyl groups,
- a C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl group, and
- 5 - a C<sub>1</sub> to C<sub>6</sub> aminoalkyl group.

In these formulae (IV) and (V), Y may also represent:



- 10 in which R<sup>8</sup> represents a polyorganosiloxane chain and T represents a group of formula:



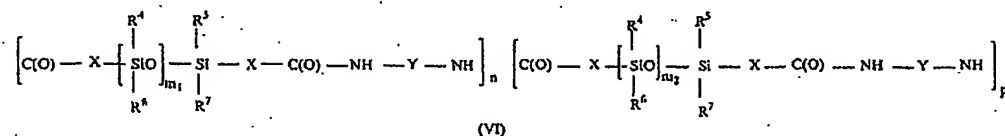
- 15 in which a, b and c are, independently, integers ranging from 1 to 10, and R<sup>13</sup> is a hydrogen atom or a group such as those defined for R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup>.

In formulae (IV) and (V), R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> preferably represent, independently, a linear or  
 20 branched C<sub>1</sub> to C<sub>40</sub> alkyl group, preferably a CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub> or isopropyl group, a polyorganosiloxane chain or

a phenyl group optionally substituted with one to three methyl or ethyl groups.

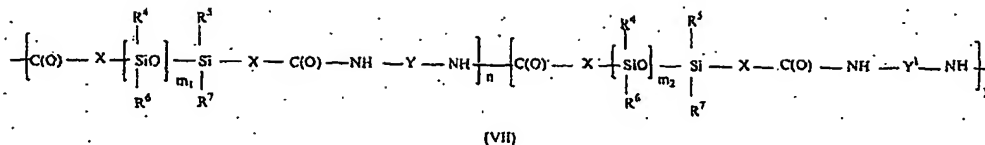
As has been seen previously, the polymer may comprise identical or different moieties of formula (IV) or (V).

Thus, the polymer may be a polyamide containing several moieties of formula (IV) or (V) of different lengths, i.e. a polyamide corresponding to the formula:



in which X, Y, n and R<sup>4</sup> to R<sup>7</sup> have the meanings given above, m<sub>1</sub> and m<sub>2</sub>, which are different, are chosen in the range from 1 to 1 000, and p is an integer ranging from 2 to 300.

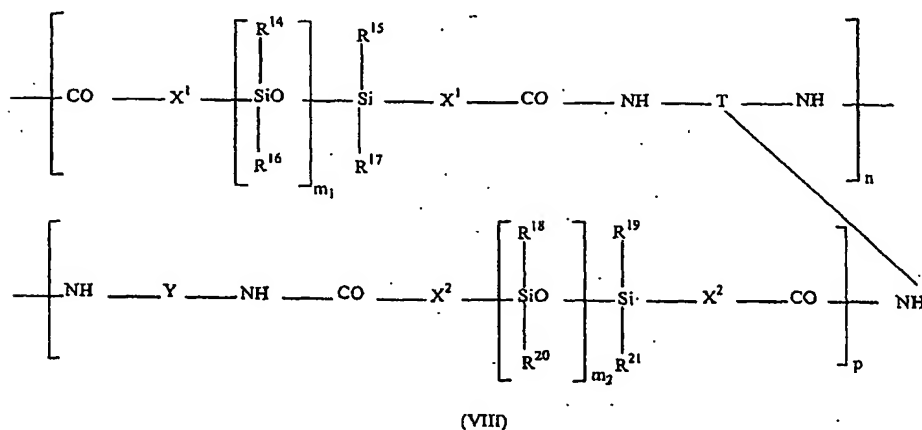
In this formula, the moieties may be structured to form either a block copolymer, or a random copolymer or an alternating copolymer. In this copolymer, the moieties may be not only of different lengths, but also of different chemical structures, for example containing different groups Y. In this case, the copolymer may correspond to the formula:



in which  $R^4$  to  $R^7$ ,  $X$ ,  $Y$ ,  $m_1$ ,  $m_2$ ,  $n$  and  $p$  have the meanings given above and  $Y^1$  is different from  $Y$  but chosen from the groups defined for  $Y$ . As previously, the various moieties may be structured to form either a block copolymer, or a random copolymer or an alternating copolymer.

In this first embodiment of the invention, the structuring agent may also consist of a graft copolymer. Thus, the polyamide containing silicone units may be grafted and optionally crosslinked with silicone chains containing amide groups. Such polymers may be synthesized with trifunctional amines.

In this case, the copolymer may comprise at least one moiety of formula:

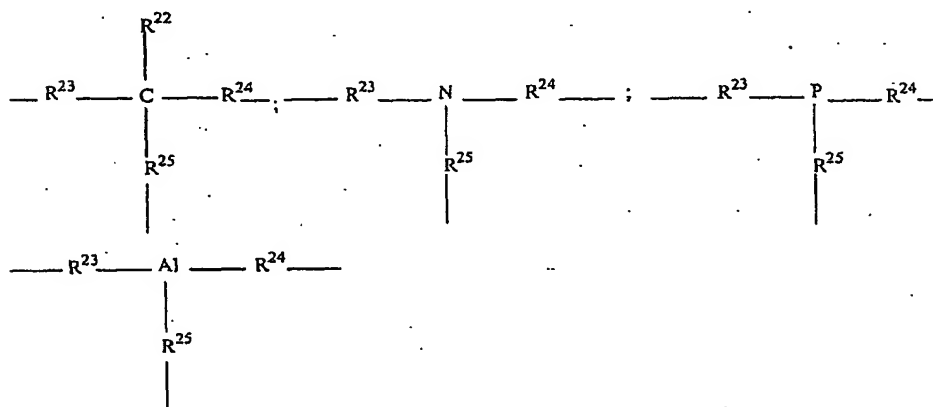




in which  $X^1$  and  $X^2$ , which are identical or different, have the meaning given for  $X$  in formula (II),  $n$  is as defined in formula (II),  $Y$  and  $T$  are as defined in formula (II),  $R^{14}$  to  $R^{21}$  are groups chosen from the same group as  $R^4$  to  $R^7$ ,  $m_1$  and  $m_2$  are numbers in the range from 1 to 1 000, and  $p$  is an integer ranging from 2 to 500.

In formula (VIII), it is preferred that:

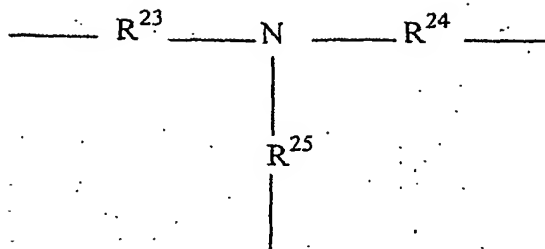
- 10        -  $p$  is in the range from 1 to 25 and better still from 1 to 7,  
           -  $R^{14}$  to  $R^{21}$  are methyl groups,  
           -  $T$  corresponds to one of the following formulae:



15

in which  $R^{22}$  is a hydrogen atom or a group chosen from the groups defined for  $R^4$  to  $R^7$ , and  $R^{23}$ ,  $R^{24}$  and  $R^{25}$  are, independently, linear or branched alkylene groups, and  
 20 more preferably corresponds to the formula:

45



in particular with  $R^{23}$ ,  $R^{24}$  and  $R^{25}$  representing

5 -CH<sub>2</sub>-CH<sub>2</sub>-,

-  $m_1$  and  $m_2$  are in the range from 15 to 500 and better still from 15 to 45,

-  $X^1$  and  $X^2$  represent -(CH<sub>2</sub>)<sub>10</sub>-, and

- Y represents -CH<sub>2</sub>-.

10 These polyamides containing a grafted silicone moiety of formula (VIII) may be copolymerized with polyamide-silicones of formula (III) to form block copolymers, alternating copolymers or random copolymers. The weight percentage of grafted silicone  
15 moieties (VIII) in the copolymer may range from 0.5% to 30% by weight.

According to the invention, as has been seen previously, the siloxane units may be in the main chain or backbone of the polymer, but they may also be  
20 present in grafted or pendent chains. In the main chain, the siloxane units may be in the form of segments as described above. In the pendent or grafted

chains, the siloxane units may appear individually or in segments.

According to the invention, the preferred siloxane-based polyamides are:

- 5        - polyamides of formula (IV) in which  $m$  is from 15 to 50;
- polyamides of formula (IV) in which  $m$  is from 30 to 500;
- mixtures of two or more polyamides in which at  
10    least one polyamide has a value of  $m$  in the range from 15 to 50 and at least one polyamide has a value of  $m$  in the range from 30 to 50;
- polymers of formula (VI) with  $m_1$  chosen in the range from 15 to 50 and  $m_2$  chosen in the range from 30  
15    to 500 with the portion corresponding to  $m_1$  representing 1% to 99% by weight of the total weight of the polyamide and the portion corresponding to  $m_2$  representing 1% to 99% by weight of the total weight of the polyamide;
- 20        - mixtures of polyamide of formula (IV) combining
  - 1) 80% to 99% by weight of a polyamide in which  $n$  is equal to 2 to 10 and in particular 3 to 6, and
  - 2) 1% to 20% of a polyamide in which  $n$  is in the range from 30 to 500 and in particular from 30 to 100,
- 25        - mixtures of polyamide of formula (IV) combining
  - 1) 1% to 20% by weight of a polyamide in which  $n$  is equal to 2 to 10 and in particular 3 to 6, and

2) 80% to 99% of a polyamide in which  $n$  is in the range from 30 to 500 and in particular from 30 to 100;

- polyamides corresponding to formula (VII) in which at least one of the groups  $Y$  and  $Y^1$  contains at least one hydroxyl substituent;

- polyamides of formula (IV) synthesized with at least one portion of an activated diacid (diacid chloride, dianhydride or diester) instead of the diacid;

- polyamides of formula (IV) in which  $X$  represents  $-(CH_2)_3-$  or  $-(CH_2)_{10}-$  and

- polyamides of formula (IV) in which the polyamides end with a monofunctional chain chosen from the group consisting of monofunctional amines, monofunctional acids, monofunctional alcohols, including fatty acids, fatty alcohols and fatty amines, such as, for example, octylamine, octanol, stearic acid and stearyl alcohol.

According to the invention, the ends of the polymer chains may end with:

- a  $C_1$  to  $C_{50}$  alkyl ester group by introducing a  $C_1$  to  $C_{50}$  monoalcohol during the synthesis,

- a  $C_1$  to  $C_{50}$  alkylamide group by taking as stopping group a monoacid if the silicone is  $\alpha,\omega$ -diaminated, or a monoamine if the silicone is an  $\alpha,\omega$ -dicarboxylic acid.

According to one embodiment variant of the invention, it is possible to use a copolymer of silicone polyamide and of hydrocarbon-based polyamide, i.e. a copolymer comprising moieties of formula (IV) or (V) and hydrocarbon-based polyamide moieties. In this case, the polyamide-silicone moieties may be arranged at the ends of the hydrocarbon-based polyamide.

Polyamide-based structuring agents containing silicones may be produced by silylic amidation of polyamides based on fatty acid dimer. This approach involves the reaction of free acid sites existing on a polyamide as end sites, with oligosiloxane-monoamines and/or oligosiloxane-diamines (amidation reaction), or alternatively with oligosiloxane alcohols or oligosiloxane diols (esterification reaction). The esterification reaction requires the presence of acid catalysts, as is known in the art. It is desirable for the polyamide containing free acid sites, used for the amidation or esterification reaction, to have a relatively high number of acid end groups (for example polyamides with high acid numbers, for example from 15 to 20).

For the amidation of the free acid sites of the hydrocarbon-based polyamides, siloxane diamines with 1 to 300, more particularly 2 to 50 and better still 2, 6, 9.5, 12, 13.5, 23 or 31 siloxane groups, may be used for the reaction with hydrocarbon-based

polyamides based on fatty acid dimers. Siloxane diamines containing 13.5 siloxane groups are preferred, and the best results are obtained with the siloxane diamine containing 13.5 siloxane groups and polyamides containing high numbers of carboxylic acid end groups.

The reactions may be carried out in xylene to extract the water produced from the solution by azeotropic distillation, or at higher temperatures (about 180 to 200°C) without solvent. Typically, the efficacy of the amidation and the reaction rates decrease when the siloxane diamine is longer, that is to say when the number of siloxane groups is higher. Free amine sites may be blocked after the initial amidation reaction of the diaminosiloxanes by reacting them either with a siloxane acid, or with an organic acid such as benzoic acid.

For the esterification of the free acid sites on the polyamides, this may be performed in boiling xylene with about 1% by weight, relative to the total weight of the reagents, of para-toluenesulphonic acid as catalyst.

These reactions carried out on the carboxylic acid end groups of the polyamide lead to the incorporation of silicone moieties only at the ends of the polymer chain.

It is also possible to prepare a copolymer of polyamide-silicone, using a polyamide containing free

amine groups, by amidation reaction with a siloxane containing an acid group.

It is also possible to prepare a structuring agent based on a copolymer between a hydrocarbon-based polyamide and a silicone polyamide, by transamidation of a polyamide having, for example, an ethylenediamine constituent, with an oligosiloxane- $\alpha,\omega$ -diamine, at high temperature (for example 200 to 300°C), to carry out a transamidation such that the ethylenediamine component of the original polyamide is replaced with the oligosiloxane diamine.

The copolymer of hydrocarbon-based polyamide and of polyamide-silicone may also be a graft copolymer comprising a hydrocarbon-based polyamide backbone with pendent oligosiloxane groups.

This may be obtained, for example:

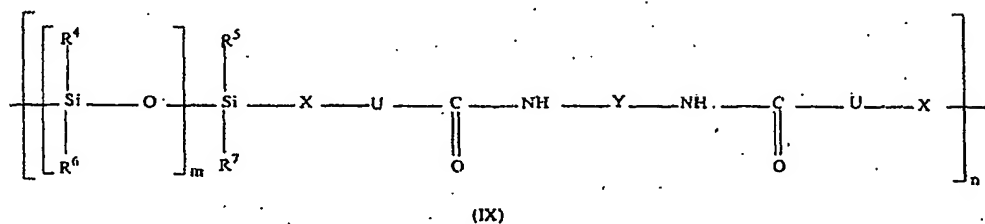
- by hydrosilylation of unsaturated bonds in polyamides based on fatty acid dimers;
- by silylation of the amide groups of a polyamide; or
- by silylation of unsaturated polyamides by means of an oxidation, that is to say by oxidizing the unsaturated groups into alcohols or diols, to form hydroxyl groups that are reacted with siloxane carboxylic acids or siloxane alcohols. The olefinic sites of the unsaturated polyamides may also be

epoxidized and the epoxy groups may then be reacted with siloxane amines or siloxane alcohols.

According to a second embodiment of the invention, the structuring agent consists of a homopolymer or a copolymer comprising urethane or urea groups.

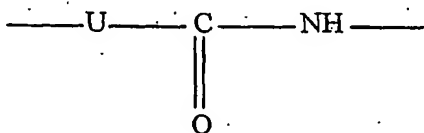
As previously, the polymer may comprise polyorganosiloxane moieties containing two or more urethane and/or urea groups, either in the backbone of the polymer or on side chains or as pendent groups.

The polymers comprising at least two urethane and/or urea groups in the backbone may be polymers comprising at least one moiety corresponding to the following formula (IX):



in which  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $X$ ,  $Y$ ,  $m$  and  $n$  have the meanings given above for formula (II), and  $U$  represents  $\text{-O-}$  or

$\text{-NH-}$ , such that:





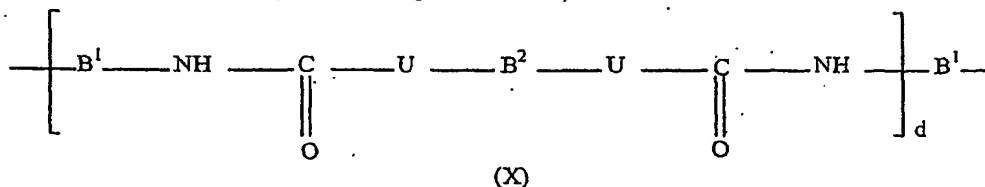
corresponds to a urethane or urea group.

In this formula (IX), Y may be a linear or branched C<sub>1</sub> to C<sub>40</sub> alkylene group, optionally substituted with a C<sub>1</sub> to C<sub>15</sub> alkyl group or a C<sub>5</sub> to C<sub>10</sub> aryl group. Preferably, a -(CH<sub>2</sub>)<sub>6</sub>- group is used.

Y may also represent a C<sub>5</sub> to C<sub>12</sub> cycloaliphatic or aromatic group that may be substituted with a C<sub>1</sub> to C<sub>15</sub> alkyl group or a C<sub>5</sub> to C<sub>10</sub> aryl group, for example a radical chosen from the methylene-4,4-biscyclohexyl radical, the radical derived from isophorone diisocyanate, 2,4- and 2,6-tolyls, 1,5-naphthylene, p-phenylene and 4,4'-biphenylenemethane. Generally, it is preferred for Y to represent a linear or branched C<sub>1</sub> to C<sub>40</sub> alkylene radical or a C<sub>4</sub> to C<sub>12</sub> cycloalkylene radical.

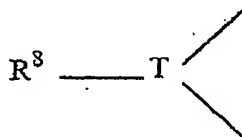
Y may also represent a polyurethane or polyurea block corresponding to the condensation of several diisocyanate molecules with one or more molecules of coupling agents of the diol or diamine type. In this case, Y comprises several urethane or urea groups in the alkylene chain:

It may correspond to the formula (X):



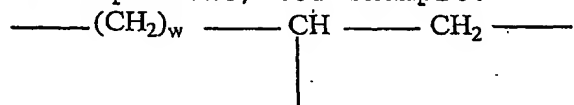
in which  $B^1$  is a group chosen from the groups given above for Y, U is -O- or -NH- and  $B^2$  is chosen from:

- linear or branched  $C_1$  to  $C_{40}$  alkylene groups,
  - $C_5$  to  $C_{12}$  cycloalkylene groups, optionally
- 5 bearing alkyl substituents, for example one to three methyl or ethyl groups, or alkylene substituents, for example the diol radical: cyclohexanedimethanol,
- phenylene groups that may optionally bear  $C_1$  to  $C_3$  alkyl substituents, and
- 10 • groups of formula:



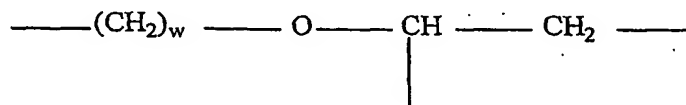
in which T is a hydrocarbon-based trivalent radical possibly containing one or more heteroatoms such as oxygen, sulphur and nitrogen and  $R^8$  is a polyorganosiloxane chain or a linear or branched  $C_1$  to  $C_{50}$  alkyl chain.

T can represent, for example:



20

or

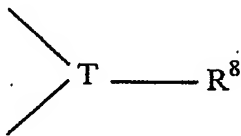


with w being an integer ranging from 1 to 10 and  $R^8$  being a polyorganosiloxane chain.

When Y is a linear or branched  $C_1$  to  $C_{40}$  alkylene group, the  $-(CH_2)_2-$  and  $-(CH_2)_6-$  groups are preferred.

In the formula given above for Y, d may be an integer ranging from 0 to 5, preferably from 0 to 3 and more preferably equal to 1 or 2.

Preferably,  $B^2$  is a linear or branched  $C_1$  to  $C_{40}$  alkylene group, in particular  $-(CH_2)_2-$  or  $-(CH_2)_6-$  or the group:



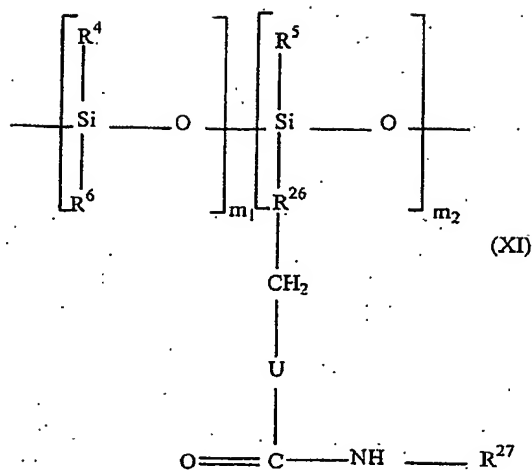
with  $R^8$  being a polyorganosiloxane chain.

As previously, the polymer constituting the structuring agent may be formed from silicone urethane and/or silicone urea moieties of different length and/or constitution, and may be in the form of block or random copolymers.

According to the invention, the silicone may also comprise urethane and/or urea groups no longer in the backbone but as side branches.

In this case, the polymer may comprise at least one moiety of formula:

55



in which  $R^4$ ,  $R^5$ ,  $R^6$ ,  $m_1$  and  $m_2$  have the meanings given above for formula (II),

- 5        - U represents O or NH,  
       -  $R^{26}$  represents a  $C_1$  to  $C_{40}$  alkylene group, optionally comprising one or more heteroatoms chosen from O and N, or a phenylene group, and  
       -  $R^{27}$  is chosen from linear, branched or cyclic,  
 10       saturated or unsaturated  $C_1$  to  $C_{50}$  alkyl groups, and phenyl groups optionally substituted with one to three  $C_1$  to  $C_3$  alkyl groups.

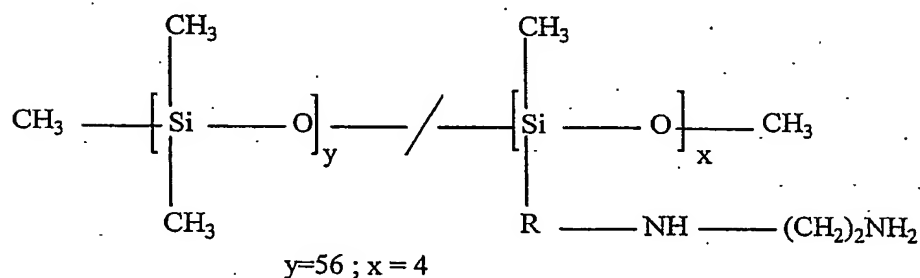
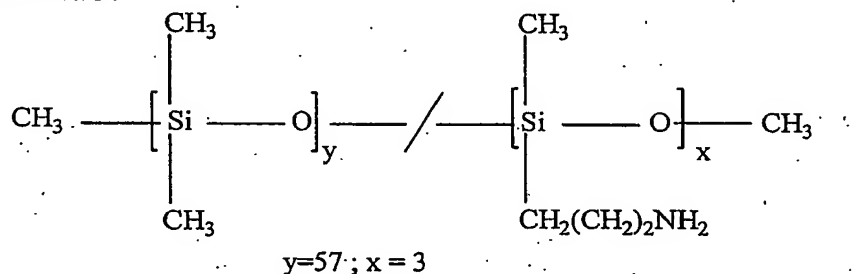
The polymers comprising at least one moiety of formula (XI) contain siloxane units and urea or  
 15       urethane groups, and they may be used as structuring agents in the compositions of the invention.

The siloxane polymers may have a single urea or urethane group per branch or may have branches containing two urea or urethane groups, or

alternatively they may contain a mixture of branches containing one urea or urethane group and branches containing two urea or urethane groups.

They may be obtained from branched polysiloxanes, comprising one or two amino groups per branch, by reacting these polysiloxanes with monoisocyanates.

As examples of starting polymers of this type containing amino and diamino branches, mention may be made of the polymers corresponding to the following formulae:



In these formulae, the symbol "/" indicates that the segments may be of different lengths and in a random order, and R represents a linear aliphatic group preferably containing 1 to 6 carbon atoms and better still 1 to 3 carbon atoms.

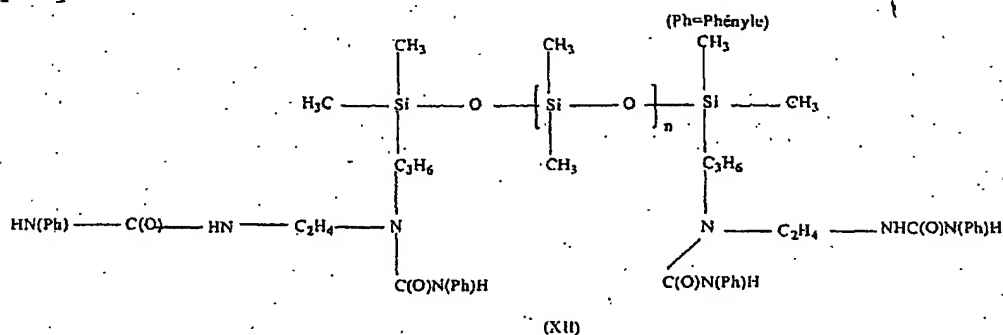
Such polymers containing branching may be formed by reacting a siloxane polymer, containing at least three amino groups per polymer molecule, with a compound containing only one monofunctional group (for example an acid, an isocyanate or an isothiocyanate) to react this monofunctional group with one of the amino groups and to form the groups capable of establishing hydrogen interactions. The amino groups may be on side chains extending from the main chain of the siloxane polymer, such that the groups capable of establishing hydrogen interactions are formed on these side chains, or alternatively the amino groups may be at the ends of the main chain, such that the groups capable of hydrogen interaction will be end groups of the polymer.

As a procedure for forming a polymer containing siloxane moieties and groups capable of establishing hydrogen interactions, mention may be made of the reaction of a siloxane diamine and of a diisocyanate in a silicone solvent so as to provide a gel directly. The reaction may be performed in a silicone fluid, the resulting product being dissolved in the silicone fluid, at high temperature, the temperature of the system then being reduced to form the gel.

The polymers that are preferred for incorporation into the compositions according to the present invention are siloxane-urea copolymers that are

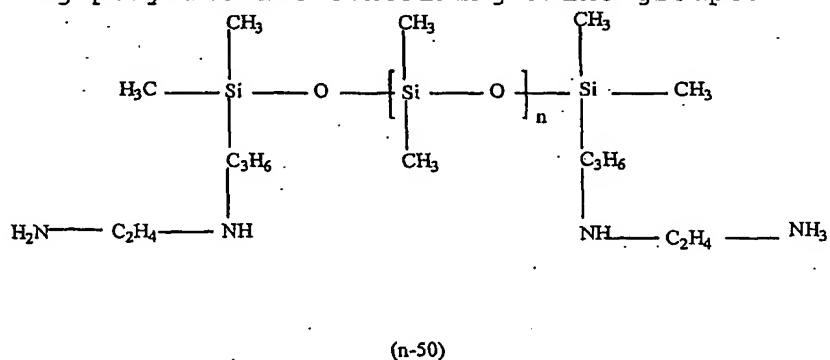
linear and that contain urea groups as groups capable of establishing hydrogen interactions in the backbone of the polymer.

As an illustration of a polysiloxane ending with four urea groups, mention may be made of the polymer of formula:



in which Ph is a phenyl group and n is a number from 0 to 300, in particular from 0 to 100, for example 50.

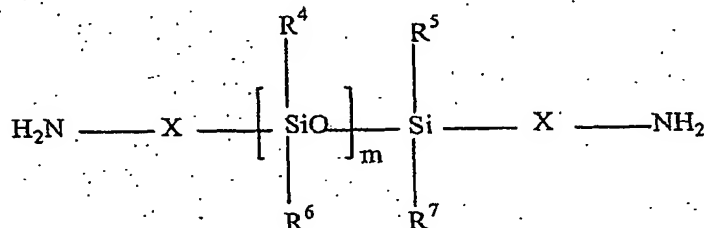
This polymer is obtained by reacting the following polysiloxane containing amino groups:



with phenyl isocyanate.

The polymers of formula (IX), comprising urea or urethane groups in the chain of the silicone polymer may be obtained by reaction between a silicone containing  $\alpha,\omega$ -NH<sub>2</sub> or -OH end groups, of formula:

5

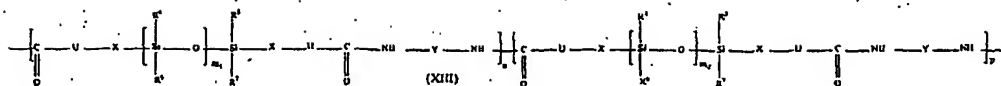


in which m, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and X are as defined for formula (II), and a diisocyanate OCN-Y-NCO in which Y  
10 has the meaning given in formula (II); and optionally a diol or diamine coupling agent of formula H<sub>2</sub>N-B<sup>2</sup>-NH<sub>2</sub> or HO-B<sup>2</sup>-OH, in which B<sup>2</sup> is as defined in formula (X).

According to the stoichiometric proportions between the two reagents, diisocyanate and coupling  
15 agent, Y may have the formula (X) with d equal to 0 or d equal to 1 to 5.

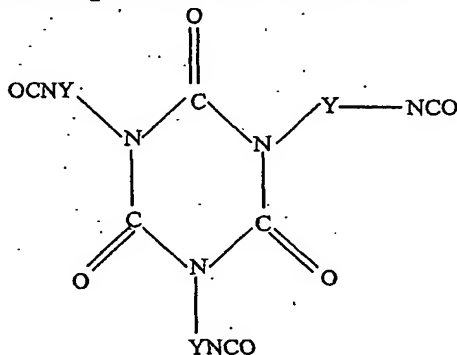
As in the case of the polyamide silicones of formula (III) or (IV), it is possible to use in the invention polyurethane or polyurea silicones containing  
20 moieties of different length and structure, in particular moieties whose lengths differ by the number of silicone moieties. In this case, the copolymer may correspond, for example, to the formula:





in which  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ ,  $\text{X}$ ,  $\text{Y}$  and  $\text{U}$  are as defined for  
 5 formula (IX) and  $m_1$ ,  $m_2$ ,  $n$  and  $p$  are as defined for  
 formula (VI).

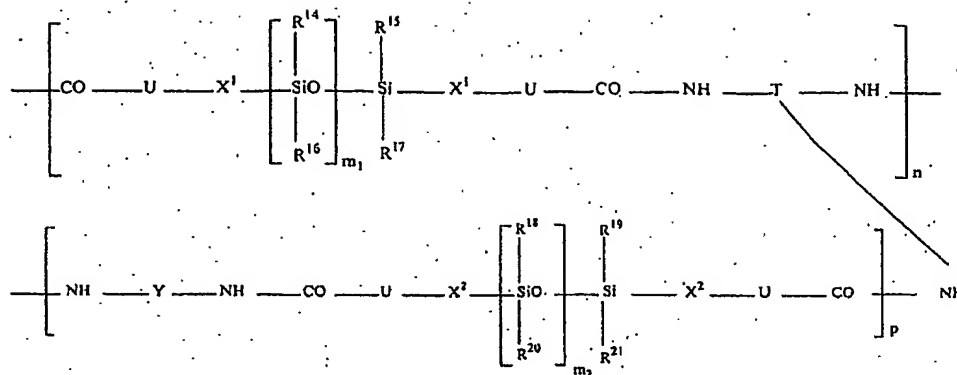
Branched polyurethane or polyurea silicones  
 may also be obtained using, instead of the diisocyanate  
 $\text{OCN}-\text{Y}-\text{NCO}$ , a triisocyanate of formula:



10

A polyurethane or polyurea silicone  
 containing branches comprising an organosiloxane chain  
 with groups capable of establishing hydrogen  
 interactions is thus obtained. Such a polymer  
 15 comprises, for example, a moiety corresponding to the  
 formula:

61



(XIV)

in which  $\text{X}^1$  and  $\text{X}^2$ , which are identical or different, have the meaning given for X in formula (II), n is as defined in formula (II), Y and T are as defined in formula (II),  $\text{R}^{14}$  to  $\text{R}^{21}$  are groups chosen from the same group as  $\text{R}^4$  to  $\text{R}^7$ ,  $m_1$  and  $m_2$  are numbers in the range from 1 to 1 000, and p is an integer ranging from 2 to 500.

As in the case of the polyamides, this copolymer can also comprise polyurethane silicone moieties without branching.

In this second embodiment of the invention, the siloxane-based polyureas and polyurethanes that are preferred are:

- polymers of formula (IX) in which m is from 15 to 50;
- polymers of formula (IX) in which m is from 30 to 500;

- mixtures of two or more polymers in which at least one polymer has a value of  $m$  in the range from 15 to 50 and at least one polymer has a value of  $m$  in the range from 30 to 50;
- 5       - polymers of formula (XIII) with  $m_1$  chosen in the range from 15 to 50 and  $m_2$  chosen in the range from 30 to 500 with the portion corresponding to  $m_1$  representing 1% to 99% by weight of the total weight of the polymer and the portion corresponding to  $m_2$  representing 1% to  
10   99% by weight of the total weight of the polymer;
  - mixtures of polymer of formula (IX) combining
    - 1) 80% to 99% by weight of a polymer in which  $n$  is equal to 2 to 10 and in particular 3 to 6, and
    - 2) 1% to 20% of a polymer in which  $n$  is in the  
15   range from 30 to 500 and in particular from 30 to 100,
  - mixtures of polymer of formula (IX) combining
    - 1) 1% to 20% by weight of a polymer in which  $n$  is equal to 2 to 10 and in particular 3 to 6, and
    - 2) 80% to 99% of a polymer in which  $n$  is in the  
20   range from 30 to 500 and in particular from 30 to 100;
  - copolymers comprising two moieties of formula (IX) in which at least one of the groups  $Y$  contains at least one hydroxyl substituent;
  - polymers of formula (IX) synthesized with at  
25   least one portion of an activated diacid (diacid chloride, dianhydride or diester) instead of the diacid;

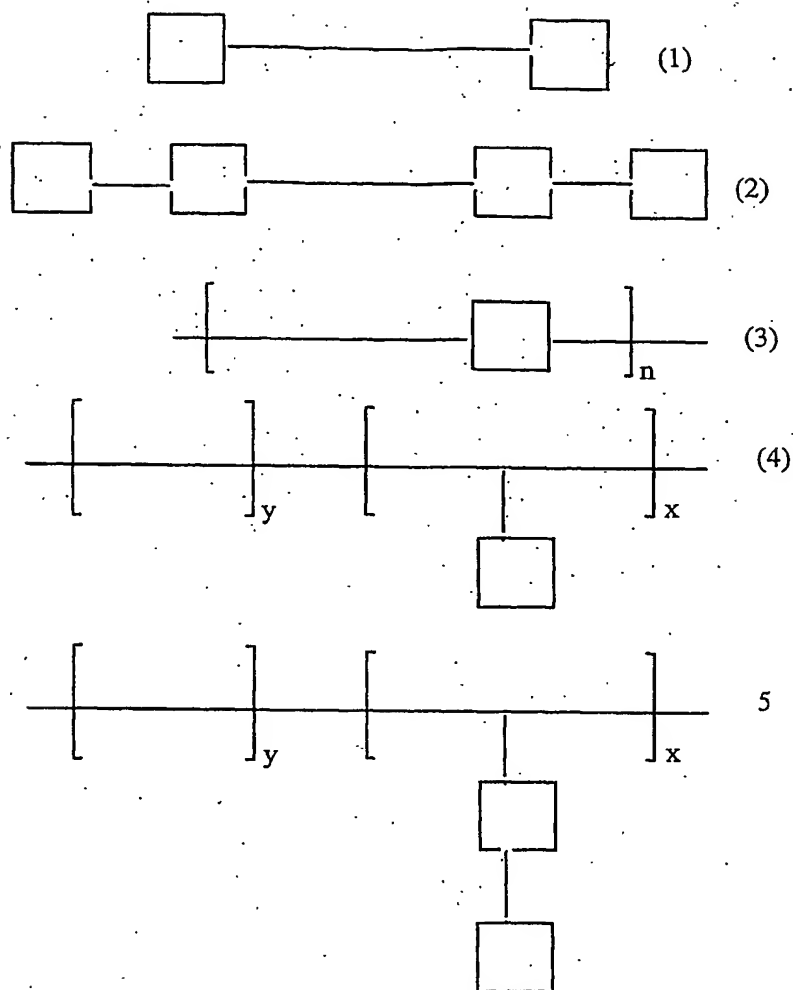
- polymers of formula (IX) in which X represents  
- (CH<sub>2</sub>)<sub>3</sub>- or - (CH<sub>2</sub>)<sub>10</sub>-; and

- polymers of formula (IX) in which the polymers  
end with a monofunctional chain chosen from the group  
5 consisting of monofunctional amines, monofunctional  
acids, monofunctional alcohols, including fatty acids,  
fatty alcohols and fatty amines, such as, for example,  
octylamine, octanol, stearic acid and stearyl alcohol.

As in the case of the polyamides, copolymers  
10 of polyurethane or polyurea silicone and of  
hydrocarbon-based polyurethane or polyurea may be used  
in the invention by performing the reaction for  
synthesizing the polymer in the presence of an  $\alpha,\omega$ -  
difunctional block of non-silicone nature, for example  
15 a polyester, a polyether or a polyolefin.

As has been seen previously, structuring  
agents consisting of homopolymers or copolymers of the  
invention may contain siloxane moieties in the main  
chain of the polymer and groups capable of establishing  
20 hydrogen interactions, either in the main chain of the  
polymer or at the ends thereof, or on side chains or  
branches of the main chain. This may correspond to the  
following five arrangements:

64



in which the continuous line is the main chain of the siloxane polymer and the squares represent the groups capable of establishing hydrogen interactions.

In case (1), the groups capable of establishing hydrogen interactions are arranged at the ends of the main chain. In case (2), two groups capable of establishing hydrogen interactions are arranged at each of the ends of the main chain.

In case (3), the groups capable of establishing hydrogen interactions are arranged within the main chain in repeating moieties.

In cases (4) and (5), these are copolymers in which the groups capable of establishing hydrogen interactions are arranged on branches of the main chain of a first series of moieties that are copolymerized with moieties not comprising groups capable of establishing hydrogen interactions. The values n, x and y are such that the polymer has the desired properties in terms of an agent for structuring fatty phases based on silicone oil.

According to the invention, the structuring of the liquid fatty phase containing at least one ester oil, is obtained with the aid of one or more of the polymers mentioned above.

As examples of polymers that may be used, mention may be made of the silicone polyamides obtained in accordance with Examples 1 to 3 of document US-A-5 981 680.

The structuring polymers and copolymers used in the composition of the invention advantageously have a softening point from 65°C to 190°C. Preferably, they have a softening point ranging from 70 to 130°C and better still from 80°C to 105°C. This softening point is lower than that of the other known structuring polymers, which facilitates the use of the polymers

described above, allows the use of volatile oils and limits the deteriorations of the liquid fatty phase.

They have good solubility in silicone oils and ester oils and produce macroscopically homogeneous compositions. Preferably, they have an average molecular mass from 500 to 200 000, for example from 1 000 to 100 000, preferably from 2 000 to 30 000.

The quantities of the ester ("short" ester) oil(s) and of the structuring polymer(s) may be chosen according to the desired texture or hardness and the desired stability of the compositions and according to the specific application envisaged. The respective quantities of the (at least one) structuring polymer and of the short ester(s) may be such that a disintegratable solid which does not run under the effects of its own weight is obtained.

According to the invention, the composition preferably has a hardness ranging from 20 to 2 000 gf and better still from 20 to 900 gf, particularly from 20 to 600 gf, and for example from 150 to 450 gf. This hardness may be measured according to a method of penetration of a probe into the said composition and in particular with the aid of a texture analyser (for example TA-TXT2i from Rheo) equipped with an ebonite cylinder 25 mm in height and 8 mm in diameter. The hardness measurement is carried out at 20°C at the centre of five samples of the said composition. The

cylinder is introduced into each sample of composition at a pre-speed of 2 mm/s, then at a speed of 0.5 mm/s and finally at a post-speed of 2 mm/s, the total displacement being 1 mm. The recorded hardness value is that of the maximum peak. The measurement error is  $\pm 50$  gf.

The hardness may also be measured by the "cheese wire" method, which consists in cutting a tube of lipstick 12.7 mm or 8.1 mm in diameter and in measuring the hardness at 20°C, using a DFGHS 2 tensile testing machine from the company Indelco-Chatillon, travelling at a speed of 100 mm/minute. It is expressed as the shear force (expressed in gram-force) required to cut a stick under these conditions. According to this method, the hardness of a composition in stick form according to the invention ranges from 30 to 300 gf, preferably from 30 to 250 gf and for example from 30 to 200 gf, even better from 30 to 180 gf, when the diameter of the stick is equal to 12.7 mm.

The hardness of the composition according to the invention is such that the composition is self-supporting and can disintegrate easily to form a satisfactory deposit on the skin and the lips. In addition, with this hardness, the composition of the invention shows good impact strength.

According to the invention, the composition in stick form has the behaviour of a deformable and



supple elastic solid, giving noteworthy elastic softness on application.

The respective amounts of ester oil and of silicone polymer are chosen according to the desired gel hardness and depending on the particular application envisaged. The respective quantities of polymer and of ester oil should be such that they allow the production of a self-supported composition, for example in the form of a disintegrable stick. In practice, the quantity of polymer (as active material) represents from 0.5 to 80% of the total weight of the composition, and even better from 5 to 40%.

Generally, the silicone polymer/ester oil mass ratio is in the range from 0.01 to 0.8, preferably from 0.05 to 0.5 and preferably still from 0.1 to 0.5.

The structuring silicone polymer preferably represents from 5 to 30% by weight of the composition, preferably still from 0.5 to 30% by weight, even better from 1 to 30% by weight.

#### Other additives

The composition of the invention may also comprise any ingredient usually used in the field under consideration.

Needless to say, the person skilled in the art will take care to select the optional additional ingredients and/or the amount thereof such that the

advantageous properties of the composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

The composition according to the invention  
5 may be in the form of an optionally tinted, transparent or translucent, dermatological or care composition for keratinous materials such as the skin, the lips and/or the superficial body growths, in the form of a sun protection composition, or of a make-up-removing  
10 product, in stick form or in cast form. It can especially be used as a care base for the skin, the superficial body growths or the lips (lip balms, for protecting the lips against the cold and/or sunlight and/or the wind, or a care cream for the skin, the  
15 nails or the hair).

The composition of the invention may be provided in particular in the form of a transparent or translucent rigid gel, in particular in the form of a transparent anhydrous stick.

20 The composition of the invention may also be in the form of a coloured, transparent or translucent, make-up product for the skin, in particular a foundation, optionally having care or treatment properties, a blusher, a face powder, an eyeshadow, a  
25 concealer product, an eyeliner or a make-up product for the body; a lip make-up, for instance a lipstick, a lip gloss or a pencil, optionally having care or treatment

properties; a make-up for the superficial body growths, for instance the nails or the eyelashes, in particular in the form of a mascara cake, or for the eyebrows and the hair, especially in the form of a pencil.

5           Needless to say, the composition of the invention must be cosmetically or dermatologically acceptable, that is to say that it must contain a non-toxic physiologically acceptable medium that can be applied to the skin, the superficial body growths or  
10 the lips of human beings. For the purposes of the invention, the expression "cosmetically acceptable" means a composition of pleasant appearance, odour and feel.

          According to the invention, the composition  
15 may furthermore contain colouring matter which may be chosen from lipophilic dyes, hydrophilic dyes, and mixtures thereof.

          The composition according to the invention may be manufactured by known methods, generally used in  
20 the cosmetic or dermatological field. It may be manufactured by the method which consists in heating the polymer at least to its softening point, adding thereto the oil(s), and then in mixing the whole until a clear solution is obtained. The colouring matter  
25 and/or the solid particles, and the additives are then added, with stirring. The homogeneous mixture obtained can then be cast in a suitable mould such as a lipstick

mould, or directly into the packaging articles (especially a case or dish).

The subject of the invention is also a make-up structured solid composition for the skin, the lips and/or the superficial body growths, containing at least one pigment or dye in a sufficient quantity for applying make-up to the skin, the lips and/or the superficial body growths and a liquid continuous fatty phase comprising at least one ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- 15       - at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
  - 20       - at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,
- the polymer being solid at room temperature and
- 25       soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or totally of ester oil(s),

and the pigment, the liquid fatty phase and the polymer forming a physiologically acceptable  
5 medium.

This make-up composition is preferably self-supporting.

The composition of the invention may be provided in the form of a cake mascara, an eyeliner, a  
10 foundation, a lipstick, a blusher, a make-up-removing product, a make-up product for the body, an eyeliner or a face powder, or a concealer product.

The subject of the invention is also a transparent or translucent make-up stick for the skin,  
15 the lips and/or the superficial body growths, and in particular for the lips, containing at least one pigment in a sufficient quantity for applying make-up to the skin, the lips and/or the superficial body growths and a liquid continuous fatty phase comprising  
20 an ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

25 - at least one polyorganosiloxane group,  
consisting of 1 to 1 000 organosiloxane units in

the chain of the moiety or in the form of a graft, and

- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof, the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or totally of ester oil(s) and of the pigment, the fatty phase and the polymer forming a physiologically acceptable medium.

The invention relates to a cosmetic care, make-up or treatment method for the keratinous materials of human beings, comprising the application to the keratinous materials of a cosmetic composition in accordance with the invention.

The subject of the invention is also the use of a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in

the chain of the moiety or in the form of a graft, and

- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

in a cosmetic composition or for the manufacture of a physiologically acceptable composition, containing a liquid continuous fatty phase comprising an ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, the liquid fatty phase consisting partially or totally of ester oil(s) having a flash point equal to or greater than 40°C, to structure the said composition in the form of a transparent and/or translucent self-supporting solid with a hardness ranging from 20 to 2 000 gf and preferably from 20 to 900 gf and even better from 20 to 600 gf.

The subject of invention is also the use of a continuous liquid fatty phase comprising at least one ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, essentially structured with a sufficient quantity of at least one

polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group,  
5 consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide,  
10 sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of  
15 25 to 250°C,

the liquid fatty phase consisting partially or totally of volatile oil(s) having a flash point equal to or greater than 40°C, in a cosmetic composition or for the manufacture of a physiologically  
20 acceptable, transparent or translucent and/or non-transfer and/or non-sticky composition.

The subject of the invention is also the use of a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average  
25 molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:



- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- 5 - at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,
- 10 the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,
- in a cosmetic composition or for the manufacture of a physiologically acceptable
- 15 composition, containing a liquid continuous fatty phase comprising an ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, to structure the said composition in the form of a transparent or translucent self-supporting
- 20 solid.

The subject of the invention is also the use of a continuous liquid fatty phase comprising at least one ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, essentially

25 structured with a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-

average molecular mass ranging from 500 to 500 000,  
containing at least one moiety comprising:

- at least one polyorganosiloxane group,  
consisting of 1 to 1 000 organosiloxane units in  
a chain of the moiety or in the form of a graft,  
and
- at least two groups capable of establishing  
hydrogen interactions chosen from ester, amide,  
sulphonamide, carbamate, thiocarbamate, urea,  
urethane, thiourea, oxamido, guanidino and  
biguanidino groups, and combinations thereof,  
the polymer being solid at room temperature and  
soluble in the liquid fatty phase at a temperature of  
25 to 250°C,

the liquid fatty phase consisting partially  
or totally of volatile oil(s) having a flash point  
equal to or greater than 40°C, in a transparent or  
translucent cosmetic composition or for the manufacture  
of a transparent or translucent physiologically  
acceptable composition, as agent for improving the non-  
transfer of the composition and/or reducing the  
stickiness of the composition.

The invention also relates to the use of at  
least one ester oil chosen from the esters of  
monocarboxylic acids with monoalcohols and  
polyalcohols, in the continuous liquid fatty phase of a  
cosmetic composition or for the manufacture of a

physiologically acceptable composition, the said fatty phase being essentially structured by a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group consisting of 1 to 1 000 organosiloxane units in a chain of the moiety or in the form of a graft, and

- at least two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

- the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C, so as to confer transparent or translucent properties on the said composition and/or on a deposit of the said composition on keratinous materials.

According to an advantageous characteristic of these uses, the composition has a hardness of 20 to 2 000 gf, preferably of 20 to 900 gf and even better of 20 to 600 gf.

The invention finally relates to a cosmetic method for reducing the transfer and/or the stickiness of a transparent or translucent cosmetic composition containing a liquid fatty phase comprising at least one

ester oil chosen from esters of monocarboxylic acids with monoalcohols and polyalcohols, consisting in structuring the said fatty phase with a sufficient quantity of at least one polymer (homopolymer or  
5 copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in  
10 the chain of the moiety or in the form of a graft, and

- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea,  
15 urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

20 the liquid fatty phase consisting partially or totally of ester oil(s).

The invention will now be described with reference to the following example, given by way of illustration and without limitation.

Example 1

In this example, the structuring of various oils - among which are ester oils or "short esters" used according to the invention - by a silicone polyamide PASi having a degree of polymerization of 15 (DP15) such as that of Example 3 of Patent US-5 981 680, is studied.

The structuring is studied for two silicone polyamide concentrations of 10 and 25%.

10 The procedure consists in heating in a small pan, at a temperature of 100 to 105°C or 110°C, a mixture of x% (with x = 10 or 25) of silicone polyamide and the oil to be studied, in pouring the molten mixture into a 30 ml Volga pot, and in observing, after 15 returning to the cold state, the appearance of the poured system.

The characteristics of the compositions studied and the observations made are assembled in the following Table I:

Table I

Oil	PASI concentration	
	10%	25%
Parleam	Cloudy liquid	Cloudy separated phase system
Octyldodecanol	Translucent gel	Opaque stick
Phenylated silicone	Opaque liquid	Opaque stick
Isononyl isonanoate	Transparent/translucent gel	Colourless transparent stick
Diisostearyl malate	Cloudy soft gel	Opaque stick
Isododecane	Non-homogeneous slightly cloudy liquid	Cloudy, even opaque gel
Cyclopentasiloxane	Opaque gel	Opaque hard gel
Tridecyl trimellitate	Opaque gel	Opaque gel
Caprylic/capric triglyceride	Opaque liquid	Opaque gel

For the two concentrations used, it is  
 5 observed that the silicone polyamides lead, after  
 introduction into the various oils and heating, to  
 structuring of most of the oils, that is to say to the

formation therein of cast gels or solids, such as sticks.

The observations made and presented in Table 1 clearly demonstrate that among all the oils tested, only isononyl isononanoate, which is an ester oil ("short" ester), in accordance with the invention, makes it possible to obtain not only structured systems, in the form of gels or sticks, but also systems with a transparency or translucence as defined in the present invention, for the various silicone polyamide concentrations studied.

#### Example 2

In this example, the structuring of isononyl isononanoate, which is an ester oil in accordance with the invention, is studied using a silicone polyamide similar to that of Example 1, but whose degree of polymerization is higher, namely 30, 45, 75 or 100.

The procedure used is the same as that of Example 1, that is to say that polymers with varying degrees of polymerization at concentrations of 10% to 25% and isononyl isononanoate are mixed, they are heated and they are poured into a pot and the appearance of the poured system is observed after returning to the cold state.

The characteristics of the systems studied and the observations made are assembled in the following Table II:

5

Table II

	10%	25%
DP15	Colourless transparent/ translucent gel	Colourless transparent/ translucent stick
DP30	Colourless transparent gel	Colourless transparent/ translucent stick
DP45	Colourless transparent gel	Colourless transparent/ translucent stick
DP75	Colourless transparent gel	Colourless transparent/ translucent stick
DP100	Colourless transparent gel	Colourless transparent/ translucent hard gel

Table II shows that the structuring and transparent or translucent character (as defined according to the present invention) are not lost when a

10



structured polyamide having a higher degree of polymerization is used.

The examples below demonstrate that the use, in accordance with the invention, of an isononyl isononanoate type oil makes it possible to obtain structured systems based on silicone polyamides having a variable degree of polymerization, alone or as mixtures, which have a translucent or transparent appearance.

### Example 3

In this example, a very simple formula is prepared which leads to a transparent solid system which may be provided in a pot, or even as a stick, and which may be coloured with colorants, pearlescent agents, glitter, or pigments.

The composition is prepared from the constituents below, according to the procedure of Example 1:

- |    |                              |        |
|----|------------------------------|--------|
| 20 | - Silicone polyamide of DP15 | 20%    |
|    | - Isononyl isononanoate      | qs 100 |

The cast composition obtained in the form of a "stick", with no colouring agent, is transparent for the purposes of the present invention and is colourless.

Example 4

In this example, in order to demonstrate the non-sticky and transfer-free character upon contact of the formulation according to the invention of Example 3, a stick according to the invention of identical composition is made, but by introducing colour in a concentrated manner, which masks the transparency, but makes it possible to demonstrate the transfer at the optional pressure.

The composition is prepared from the constituents below, according to the procedure of Example 1:

	- Silicone polyamide of DP15	20%
	- Isononyl isononanoate	qs 100
15	- Pigment	8.66%

The composition when applied for example to the hand is non-sticky. When the deposit is touched with the finger for example by exerting pressure, no colour is removed through contact, that is to say that no colour is transferred to the finger once the contact is terminated.

This example demonstrates that for a composition which is slightly coloured, with colorants for example, it is possible, by virtue of the invention, to obtain the transparency at the same time

as the non-stickiness and the absence of transfer  
through contact.

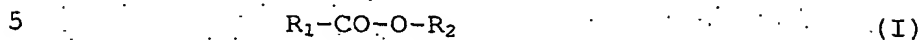
**REFERENCES**

- 5 [1] EP-A-1 068 856  
[2] WO-A-01/97758  
[3] WO-A-97 36573  
[4] US-A-5 874 069  
[5] US-A-5 919 441  
10 [6] US-A-6 051 216  
[7] WO-A-02/17870  
[8] WO-A-02/17871  
[9] EP-A-1 177 784  
[10] FR-A-2 817 740  
15 [11] FR-A-2 817 739  
[12] US-A-5 981 680  
[13] WO-A-99/06473  
[14] US-A-6 353 076

## CLAIMS

1. Care and/or make-up anhydrous cosmetic composition which is transparent or translucent, optionally capable of giving a transparent or translucent deposit, comprising:
- a liquid fatty phase comprising at least one ester oil chosen from the esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at least one polymer having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:
    - at least one polyorganosiloxane group consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
    - at least two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,
- the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C, and
- the liquid fatty phase and the structuring polymer forming a physiologically acceptable medium.
2. Care and/or make-up cosmetic composition which is transparent or translucent, optionally capable of giving a transparent or translucent deposit,

comprising a liquid fatty phase comprising at least one ester oil chosen from esters corresponding to the following formula (I):



where  $R_1$  represents a branched alkyl radical of 3 to 40 carbon atoms, preferably of 7 to 19 carbon atoms, optionally comprising one or more ethylenic double bonds, and optionally substituted,

10                       $R_2$  represents a linear or branched alkyl radical of 1 to 40 carbon atoms, preferably of 3 to 30 carbon atoms and even better of 3 to 20 carbon atoms, optionally comprising one or more ethylenic double bonds, and optionally substituted,

the said liquid phase being structured with at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

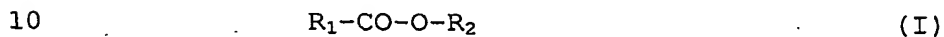
20                      - at least one polyorganosiloxane group consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and

                    - at least two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, 25 thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C, and

the liquid fatty phase and the structuring polymer forming a physiologically acceptable medium.

3. Transparent or translucent composition according to Claim 1, in which the said ester corresponds to the following formula (I):



where  $R_1$  represents a linear or branched alkyl radical of 1 to 40 carbon atoms, preferably of 7 to 19 carbon atoms, optionally comprising one or more ethylenic double bonds, and optionally substituted;

15  $R_2$  represents a linear or branched alkyl radical of 1 to 40 carbon atoms, preferably of 3 to 30 carbon atoms and even better of 3 to 20 carbon atoms, optionally comprising one or more ethylenic double bonds, and

20 optionally substituted.

4. Composition according to Claim 2 or 3, in which in formula (I),  $R_1$  represents the residue of a fatty acid comprising from 3 to 40, and even better from 7 to 19 carbon atoms, and  $R_2$  represents a linear or preferably branched hydrocarbon chain containing from 1

25 to 40, preferably from 3 to 30, and even better from 3 to 20 carbon atoms.

5. Composition according to Claim 3, in which in formula (I),  $R_1$  is a group derived from a fatty acid chosen from the group consisting of acetic, propionic, butyric, caproic, caprylic, pelargonic, capric, undecanoic, lauric, myristic, palmitic, 5 stearic, isostearic, arachidic, behenic, oleic, linolenic, linoleic, oleostearic, arachidonic and erucic acids, and mixtures thereof.

6. Composition according to Claim 2, in 10 which in formula (I),  $R_1$  represents an unsubstituted branched alkyl group of 1 to 40 carbon atoms, preferably of 7 to 19 carbon atoms; and  $R_2$  represents an unsubstituted linear or branched alkyl group of 1 to 40 carbon atoms, preferably of 3 to 30 carbon atoms and 15 even better of 3 to 20 carbon atoms, optionally comprising one or more ethylenic double bonds.

7. Composition according to Claim 5, in which in the formula (I),  $R_1$  is an unsubstituted branched alkyl group of 4 to 14 carbon atoms, 20 preferably of 8 to 10 carbon atoms, and  $R_2$  is an unsubstituted branched alkyl group of 5 to 15 carbon atoms, preferably of 9 to 11 carbon atoms.

8. Composition according to any one of Claims 2 to 6, in which in formula (I),  $R_1$ -CO- and  $R_2$  25 have the same number of carbon atoms and are derived from the same radical.

9. Composition according to any one of

Claims 2 to 7, in which in formula (I), the total number of carbon atoms of the groups  $R_1$  and  $R_2$  is greater than or equal to 9.

10. Composition according to any one of  
5 Claims 2 to 8, in which the ester oil is chosen from the following compounds:

- isononyl isononanoate,
- isostearyl isostearate,
- and mixtures thereof.

10 11. Composition according to Claim 1, in which the ester oil is chosen from the following compounds:

- cetostearyl octanoate,
- isopropyl myristate,
- 15 - 2-ethylhexyl palmitate,
- 2-octyldodecyl stearate,
- 2-octyldodecyl erucate,
- and mixtures thereof.

11. Composition according to any one of the  
20 preceding claims, in which the fatty phase comprises from 0.5 to 100% by weight, preferably from 1 to 80%, preferably still from 2 to 50% and even better from 2 to 40% of the ester oil(s).

12. Composition according to any one of  
25 Claims 1 to 10, in which the fatty phase contains, as oils, only ester oils excluding any other oil.

13. Composition according to any one of



Claims 1 to 11, in which the fatty phase contains only one ester oil which is preferably isononyl isononanoate, preferably in an amount of 100% by weight.

5           14. Composition according to any one of Claims 1 to 10 and 12, in which the liquid fatty phase comprises at least one silicone oil.

10           15. Composition according to Claim 1, in which the liquid fatty phase comprises at least one volatile oil having a flash point ranging from 35 to 135°C.

15           16. Composition according to Claim 1, in which the liquid fatty phase comprises at least one volatile oil having a vapour pressure ranging from 0.01 to 300 mmHg.

17. Composition according to Claim 14 or 15, in which the volatile oil is chosen from isododecane, isohexadecane, C<sub>8</sub>-C<sub>16</sub> isoparaffins, isohexyl neopentanoate, isodecyl neopentanoate.

20           18. Composition according to either of Claims 14 and 15, in which the volatile oil is chosen from the group consisting of the following compounds: isododecane, octyltrimethicone, hexyltrimethicone, decamethylcyclopentasiloxane D5, octamethylcyclo-  
25   tetrasiloxane D4, dodecamethylcyclohexasiloxane D6, heptamethyloctyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, polydimethylsiloxane of

1.5 cSt (25°C), polydimethylsiloxane of 2 cSt (25°C), polydimethylsiloxane of 3 cSt (25°C), polydimethylsiloxane of 5 cSt (25°C), and mixtures thereof.

19. Composition according to any one of  
5 Claims 14 to 17, in which the volatile oil is chosen from perfluoropolyethers, perfluoroalkanes, perfluoroadamantanes, esters of perfluoroalkyl phosphates and fluorinated ester oils.

20. Composition according to any one of  
10 Claims 14 to 18, in which the liquid fatty phase comprises a nonvolatile silicone oil.

21. Composition according to any one of  
Claims 13 to 19, in which the liquid fatty phase contains at least 1%, and even better at least 5% by  
15 weight, for example from 10 to 90% by weight of silicone oil(s).

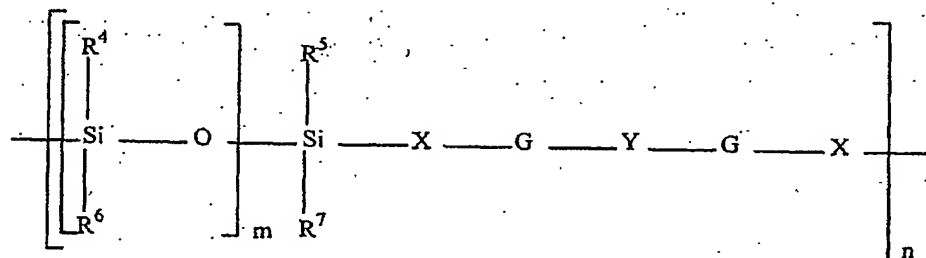
21. Composition according to any one of  
Claims 14 to 20, in which the volatile oil represents from 3 to 89.4%, preferably from 5 to 60%, for example  
20 from 5 to 10% of the total weight of the composition.

22. Composition according to any one of the preceding claims, comprising, in addition, solid particles chosen from fillers, pearlescent or non-pearlescent pigments, and mixtures thereof, in a  
25 quantity such that the composition remains transparent or translucent.

23. Composition according to Claim 22, in

which the particles are pigments chosen from zinc oxides, iron oxides, titanium oxides and mixtures thereof.

24. Composition according to any one of the preceding claims, in which the structuring polymer comprises at least one moiety corresponding to the formula:



(II)

10

in which:

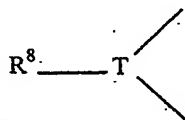
1)  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$ , which may be identical or different, represent a group chosen from:

- linear, branched or cyclic, saturated or
- 15 unsaturated,  $\text{C}_1$  to  $\text{C}_{40}$  hydrocarbon-based groups, possibly containing in their chain one or more oxygen, sulphur and/or nitrogen atoms, and possibly being partially or totally substituted with fluorine atoms,
- $\text{C}_6$  to  $\text{C}_{10}$  aryl groups, optionally substituted
- 20 with one or more  $\text{C}_1$  to  $\text{C}_4$  alkyl groups,
- polyorganosiloxane chains possibly containing one or more oxygen, sulphur and/or nitrogen atoms;

2) the groups X, which may be identical or different, represent a linear or branched C<sub>1</sub> to C<sub>30</sub> alkylenediyl group, possibly containing in its chain one or more oxygen and/or nitrogen atoms;

5 3) Y is a saturated or unsaturated, C<sub>1</sub> to C<sub>50</sub> linear or branched divalent alkylene, arylene, cycloalkylene, alkylarylene or arylalkylene group, possibly comprising one or more oxygen, sulphur and/or nitrogen atoms, and/or bearing as substituent one of  
 10 the following atoms or groups of atoms: fluorine, hydroxyl, C<sub>3</sub> to C<sub>8</sub> cycloalkyl, C<sub>1</sub> to C<sub>40</sub> alkyl, C<sub>5</sub> to C<sub>10</sub> aryl, phenyl optionally substituted with 1 to 3 C<sub>1</sub> to C<sub>3</sub> alkyl groups, C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl and C<sub>1</sub> to C<sub>6</sub> aminoalkyl, or

15 4) Y represents a group corresponding to the formula:



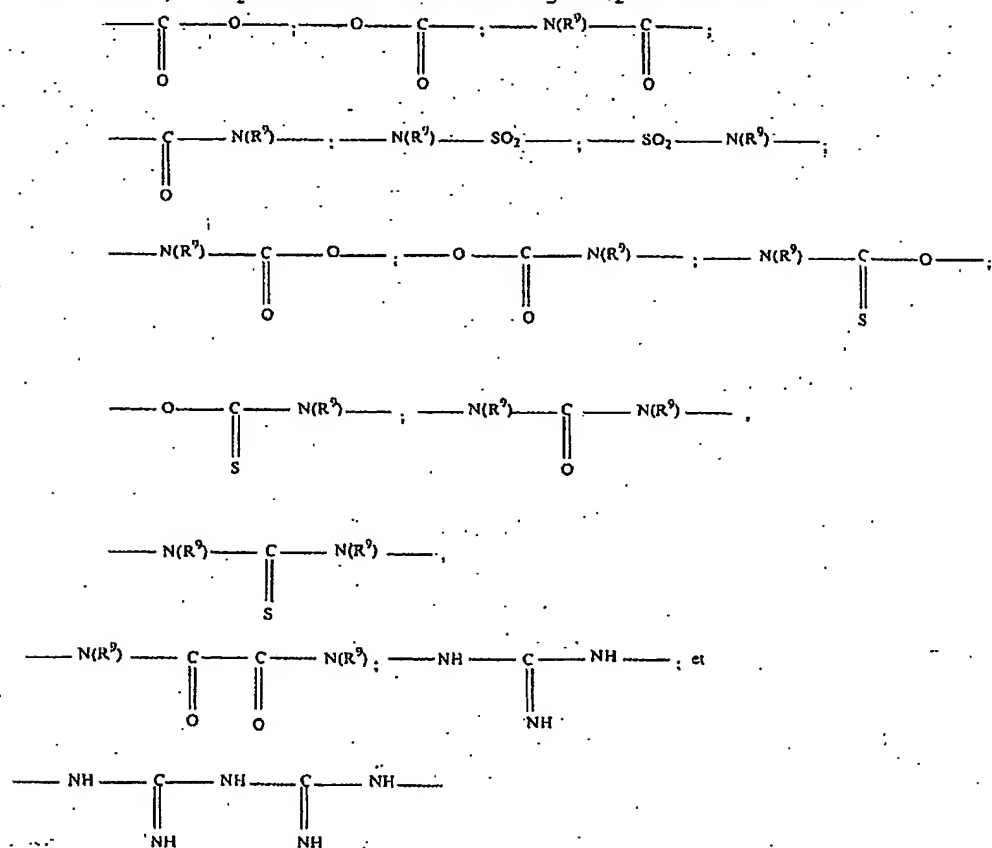
in which

20 - T represents a linear or branched, saturated or unsaturated, C<sub>3</sub> to C<sub>24</sub> trivalent or tetravalent hydrocarbon-based group optionally substituted with a polyorganosiloxane chain, and possibly containing one or more atoms chosen from O, N and S, or T represents a  
 25 trivalent atom chosen from N, P and Al, and

- R<sup>8</sup> represents a linear or branched C<sub>1</sub> to C<sub>50</sub> alkyl

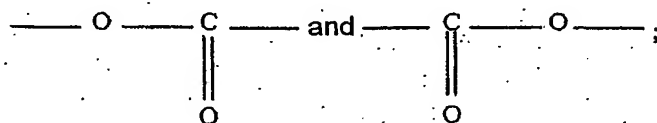
group or a polyorganosiloxane chain, possibly comprising one or more ester, amide, urethane, thiocarbamate, urea, thiourea and/or sulphonamide groups, which may possibly be linked to another chain of the polymer;

5) the groups G, which may be identical or different, represent divalent groups chosen from:



10 in which R<sup>9</sup> represents a hydrogen atom or a linear or branched C<sub>1</sub> to C<sub>20</sub> alkyl group, on condition that at least 50% of the groups R<sup>9</sup> of the polymer represent a

hydrogen atom and that at least two of the groups G of the polymer are a group other than:

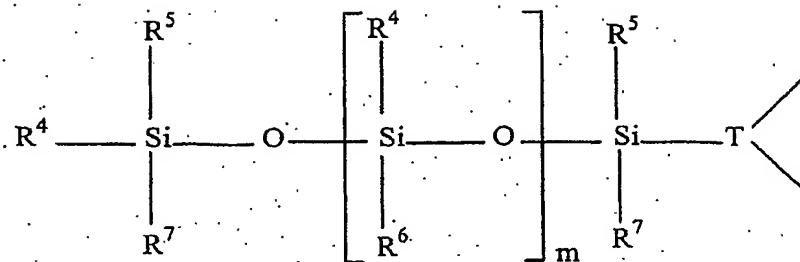


- 5            6) n is an integer ranging from 2 to 500 and preferably from 2 to 200, and m is an integer ranging from 1 to 1 000, preferably from 1 to 700 and better still from 6 to 200.

25. Composition according to Claim 24, in which Y represents a group chosen from:

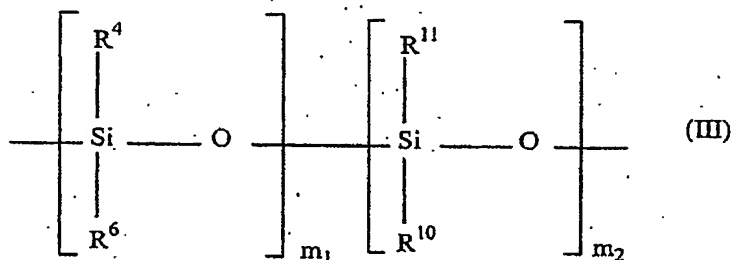
- a) linear C<sub>1</sub> to C<sub>20</sub> and preferably C<sub>1</sub> to C<sub>10</sub> alkylene groups,
- b) C<sub>30</sub> to C<sub>56</sub> branched alkylene groups possibly comprising rings and unconjugated unsaturations,
- 15        c) C<sub>5</sub>-C<sub>6</sub> cycloalkylene groups,
- d) phenylene groups optionally substituted with one or more C<sub>1</sub> to C<sub>40</sub> alkyl groups,
- e) C<sub>1</sub> to C<sub>20</sub> alkylene groups comprising from 1 to 5 amide groups,
- 20        f) C<sub>1</sub> to C<sub>20</sub> alkylene groups comprising one or more substituents chosen from hydroxyl, C<sub>3</sub> to C<sub>8</sub> cycloalkane, C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl and C<sub>1</sub> to C<sub>6</sub> alkylamine groups,
- g) polyorganosiloxane chains of formula:

98



in which  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ , T and m are as defined above in Claim 24.

26. Composition according to any one of  
 5 Claims 1 to 23, in which the structuring polymer  
 comprises at least one moiety corresponding to formula  
 (III):



10

in which

-  $\text{R}^4$  and  $\text{R}^6$ , which may be identical or different,  
 are as defined above for formula (II) in Claim 24,

-  $\text{R}^{10}$  represents a group as defined above for  $\text{R}^4$   
 15 and  $\text{R}^6$ , or represents the group of formula  $-\text{X}-\text{G}-\text{R}^{12}$  in  
 which X and G are as defined above for formula (II) in  
 Claim 24, and  $\text{R}^{12}$  represents a hydrogen atom or a  
 linear, branched or cyclic, saturated or unsaturated,  $\text{C}_1$   
 to  $\text{C}_{50}$  hydrocarbon-based group optionally comprising in

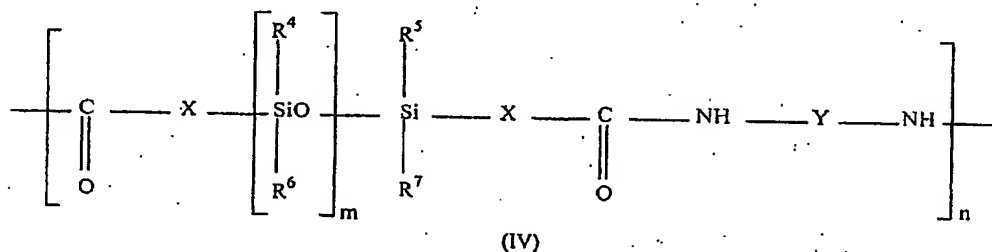
its chain one or more atoms chosen from O, S and N,  
 optionally substituted with one or more fluorine atoms  
 and/or one or more hydroxyl groups, or a phenyl group  
 optionally substituted with one or more C<sub>1</sub> to C<sub>4</sub> alkyl  
 groups,

- R<sup>11</sup> represents the group of formula -X-G-R<sup>12</sup> in  
 which X, G and R<sup>12</sup> are as defined above,

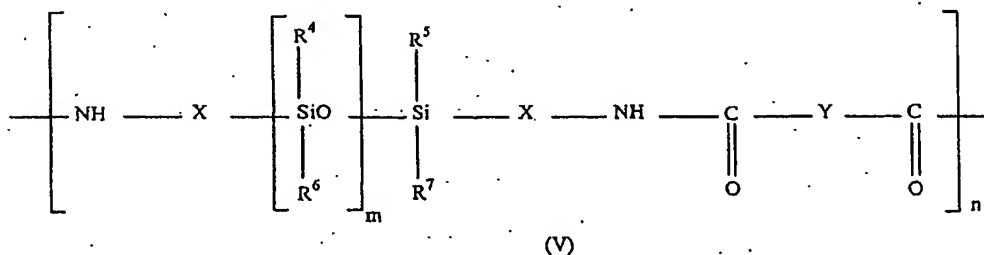
- m<sub>1</sub> is an integer ranging from 1 to 998, and

- m<sub>2</sub> is an integer ranging from 2 to 500.

27. Composition according to Claim 24, in  
 which the polymer comprises at least one moiety of  
 formula (IV) or (V):



or



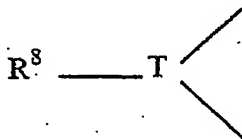
in which R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, X, Y, m and n are as defined in  
 Claim 24.



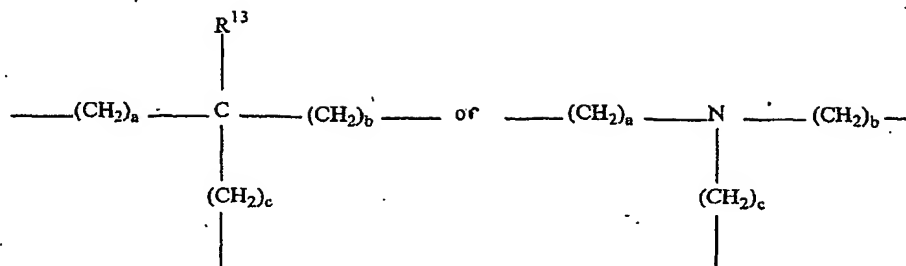
28. Composition according to either of Claims 24 and 27, in which X and/or Y represent an alkylene group containing in its alkylene portion at least one of the following elements:

- 5        1) 1 to 5 amide, urea, urethane or carbamate groups,
- 2) a C<sub>5</sub> or C<sub>6</sub> cycloalkyl group, and
- 3) a phenylene group optionally substituted with 1 to 3 identical or different C<sub>1</sub> to C<sub>3</sub> alkyl groups,
- 10      and/or substituted with at least one element chosen from the group consisting of:
  - a hydroxyl group,
  - a C<sub>3</sub> to C<sub>8</sub> cycloalkyl group,
  - one to three C<sub>1</sub> to C<sub>40</sub> alkyl groups,
  - 15      - a phenyl group optionally substituted with one to three C<sub>1</sub> to C<sub>3</sub> alkyl groups,
  - a C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl group, and
  - a C<sub>1</sub> to C<sub>6</sub> aminoalkyl group.

29. Composition according to any one of  
20 Claims 24 to 27, in which Y represents:



in which R<sup>8</sup> represents a polyorganosiloxane chain and T represents a group of formula:

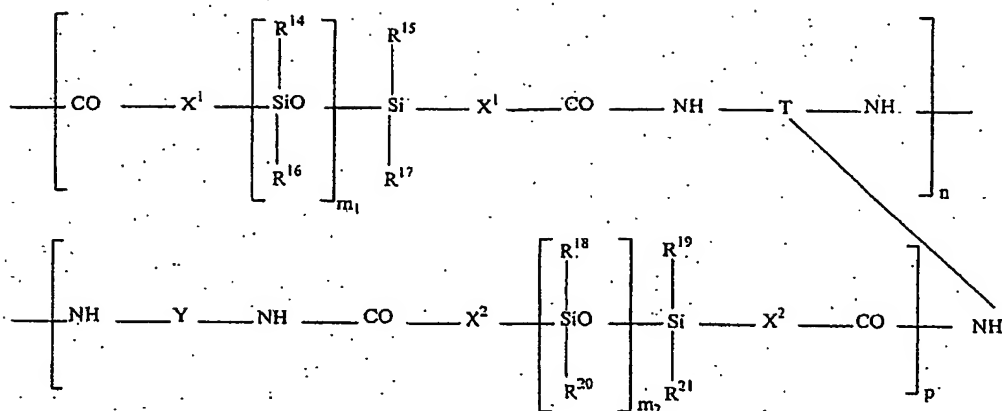


in which a, b and c are, independently, integers ranging from 1 to 10, and  $\text{R}^{13}$  is a hydrogen atom or a group such as those defined for  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$ , in  
 5 Claim 24.

30. Composition according to any one of Claims 24 to 27, in which  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  represent, independently, a linear or branched  $\text{C}_1$  to  $\text{C}_{40}$  alkyl  
 10 group, preferably a  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$  or isopropyl group, a polyorganosiloxane chain or a phenyl group optionally substituted with one to three methyl or ethyl groups.

31. Composition according to any one of Claims 1 to 23, in which the structuring polymer  
 15 comprises at least one moiety of formula:

102



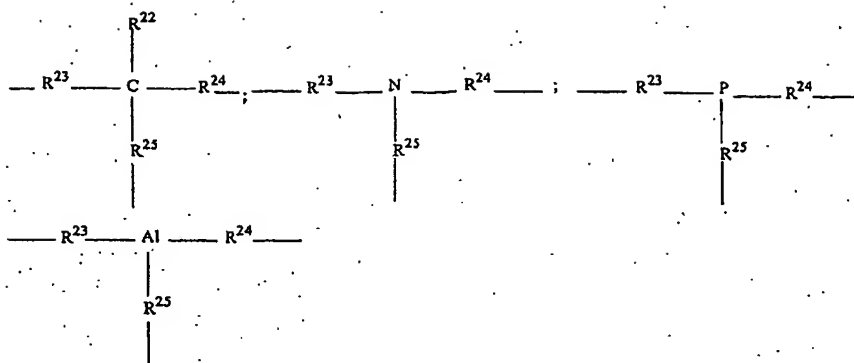
(VIII)

in which  $\text{X}^1$  and  $\text{X}^2$ , which are identical or different, have the meaning given for X in Claim 24, n, Y and T are as defined in Claim 24,  $\text{R}^{14}$  to  $\text{R}^{21}$  are groups chosen from the same group as  $\text{R}^4$  to  $\text{R}^7$  in Claim 24,  $m_1$  and  $m_2$  are numbers in the range from 1 to 1 000, and p is an integer ranging from 2 to 500.

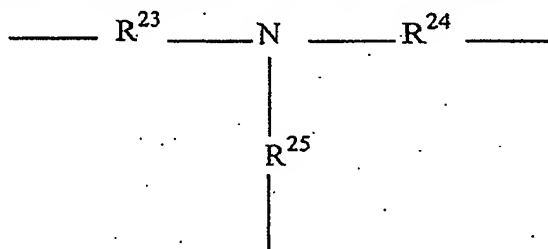
32. Composition according to Claim 31, in which:

- p is in the range from 1 to 25 and better still from 1 to 7,
- $\text{R}^{14}$  to  $\text{R}^{21}$  are methyl groups,
- T corresponds to one of the following formulae:

103



in which  $\text{R}^{22}$  is a hydrogen atom or a group chosen from the groups defined for  $\text{R}^4$  to  $\text{R}^7$ , and  $\text{R}^{23}$ ,  $\text{R}^{24}$  and  $\text{R}^{25}$  are, independently, linear or branched alkylene groups, and  
 5 more preferably correspond to the formula:

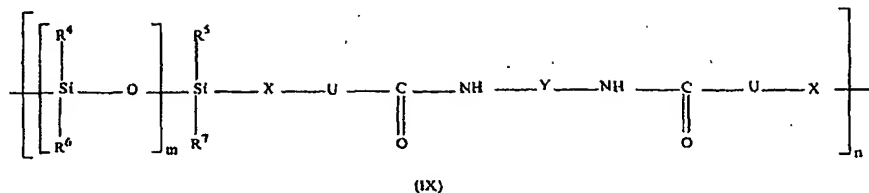


in particular with  $\text{R}^{23}$ ,  $\text{R}^{24}$  and  $\text{R}^{25}$  representing  
 $\text{---CH}_2\text{---CH}_2\text{---}$ ,

- $m_1$  and  $m_2$  are in the range from 15 to 500 and  
 10 better still from 15 to 45,
- $\text{X}^1$  and  $\text{X}^2$  represent  $\text{---(CH}_2\text{)}_{10}\text{---}$ , and
- Y represents  $\text{---CH}_2\text{---}$ .

33. Composition according to any one of Claims 1 to 23, in which the structuring polymer  
 15 comprises at least one moiety corresponding to the following formula:

104

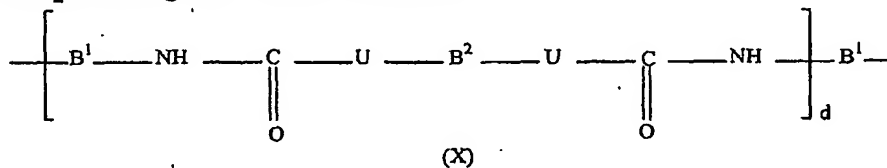


in which  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ , X, Y, m and n have the meanings given above for formula (II) in Claim 19, and U

5 represents -O- or -NH-, or

Y represents a  $C_5$  to  $C_{12}$  cycloaliphatic or aromatic group that may be substituted with a  $C_1$  to  $C_{15}$  alkyl group or a  $C_5$  to  $C_{10}$  aryl group, for example a radical chosen from the methylene-4,4-biscyclohexyl radical,  
 10 the radical derived from isophorone diisocyanate, 2,4- and 2,6-tolyls, 1,5-naphthylene, p-phenylene and 4,4'-biphenylenemethane, or Y represents a linear or branched  $C_1$  to  $C_{40}$  alkylene radical or a  $C_4$  to  $C_{12}$  cycloalkylene radical, or

15 Y represents a polyurethane or polyurea block corresponding to the condensation of several diisocyanate molecules with one or more molecules of coupling agents of the diol or diamine type, corresponding to the formula:

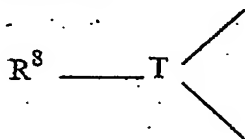


20

in which d is an integer from 0 to 5,  $B^1$  is a group

above for Y, U is -O- or -NH- and B<sup>2</sup> is chosen from:

- linear or branched C<sub>1</sub> to C<sub>40</sub> alkylene groups,
- C<sub>5</sub> to C<sub>12</sub> cycloalkylene groups, optionally bearing alkyl substituents, for example one to three methyl or ethyl groups, or alkylene substituents, for example the diol radical: cyclohexanedimethanol,
- phenylene groups that may optionally bear C<sub>1</sub> to C<sub>3</sub> alkyl substituents, and
- groups of formula:



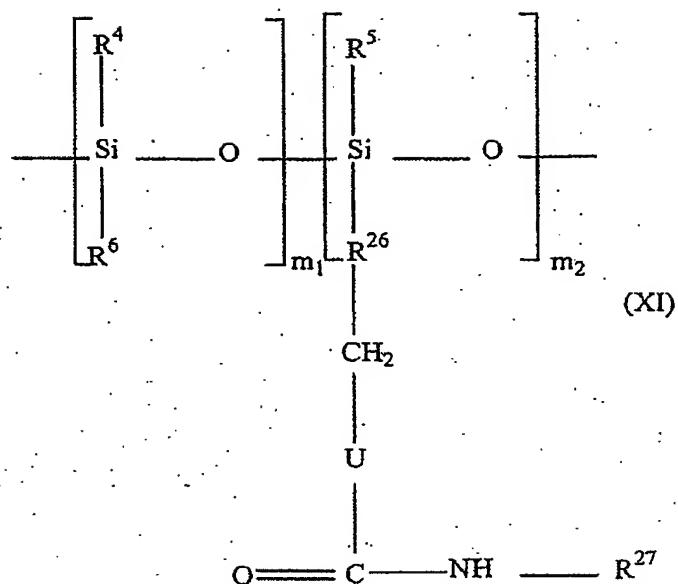
10

in which T is a hydrocarbon-based trivalent radical possibly containing one or more heteroatoms such as oxygen, sulphur and nitrogen and R<sup>8</sup> is a polyorganosiloxane chain or a linear or branched C<sub>1</sub> to C<sub>50</sub> alkyl chain.

15

34. Composition according to any one of Claims 1 to 23, in which the structuring polymer comprises at least one moiety of formula:

106



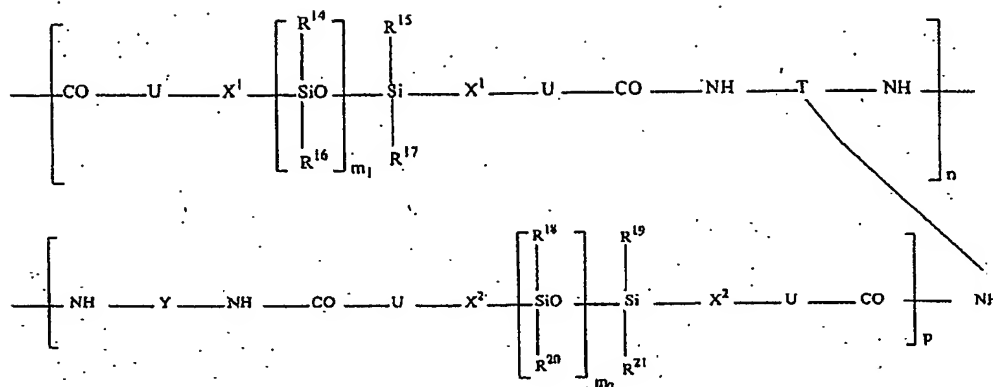
in which  $R^4$ ,  $R^5$ ,  $R^6$ ,  $m_1$  and  $m_2$  have the meanings given for formula (II) in Claim 24,

- 5           - U represents O or NH,
- $R^{26}$  represents a  $C_1$  to  $C_{40}$  alkylene group, optionally comprising one or more heteroatoms chosen from O and N, or a phenylene group, and
- $R^{27}$  is chosen from linear, branched or cyclic,
- 10   saturated or unsaturated  $C_1$  to  $C_{50}$  alkyl groups, and phenyl groups optionally substituted with one to three  $C_1$  to  $C_3$  alkyl groups.

35. Composition according to any one of Claims 1 to 23, in which the structuring polymer

15   comprises at least one moiety of formula:

107



(XIV)

in which  $\text{X}^1$  and  $\text{X}^2$ , which are identical or different, have the meaning given for X in Claim 24, n, Y and T are as defined in Claim 24,  $\text{R}^{14}$  to  $\text{R}^{21}$  are groups chosen from the same group as  $\text{R}^4$  to  $\text{R}^7$  in Claim 24,  $m_1$  and  $m_2$  are numbers in the range from 1 to 1 000, and p is an integer ranging from 2 to 500.

36. Composition according to any one of Claims 24 to 35, in which the structuring polymer further comprises at least one hydrocarbon-based moiety comprising two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof.

37. Composition according to Claim 36, in which the copolymer is a block copolymer or a graft copolymer.



38. Composition according to any one of the preceding claims, in which the structuring polymer represents from 0.5 to 80% of the total weight of the composition, preferably from 2 to 60% and even better from 5 to 40% of the total weight of the composition.

39. Composition according to any one of the preceding claims, in which the liquid fatty phase further contains a non-silicone oil.

40. Composition according to any one of the preceding claims, in which the liquid fatty phase represents from 5 to 95% of the total weight of the composition and even better from 20 to 75% of the total weight of the composition.

41. Composition according to any one of the preceding claims, characterized in that it additionally comprises colouring matter.

42. Composition according to any one of the preceding claims, characterized in that it is provided in the form of a transparent or translucent rigid gel, and in particular of a transparent anhydrous stick.

43. Transparent or translucent make-up structured solid composition for the skin, the lips and/or the superficial body growths, containing at least one pigment in a sufficient quantity for applying make-up to the skin, the lips and/or the superficial body growths and a liquid continuous fatty phase comprising at least one ester oil chosen from the

esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing  
5 at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing  
10 hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and  
15 soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or totally of ester oil(s),

and the pigment, the liquid fatty phase and the  
20 polymer forming a physiologically acceptable medium.

44. Composition according to Claim 38, characterized in that it is self-supporting.

45. Composition according to any one of Claims 1 to 44, characterized in that it is provided in  
25 the form of a cake mascara, an eyeliner, a foundation, a lipstick, a blusher, a make-up-removing product, a make-up product for the body, an eyeshadow or a face

powder, or a concealer product.

46. Transparent or translucent make-up stick for the skin, the lips and/or the superficial body growths, and in particular for the lips, containing at least one pigment in a sufficient quantity for applying make-up to the skin, the lips and/or the superficial body growths and a liquid continuous fatty phase comprising an ester oil chosen from the esters of monocarboxylic acids with monoalcohols and polyalcohols, structured with at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or totally of ester oil(s) and the pigment, the fatty phase and the polymer forming a physiologically

acceptable medium.

47. Cosmetic care, make-up or treatment method for the keratinous materials of human beings, comprising the application to the keratinous materials of a cosmetic composition according to one of the preceding claims.

48. Use of a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

in a cosmetic composition or for the manufacture of a physiologically acceptable composition, containing a liquid continuous fatty phase comprising an ester oil chosen from the esters of monocarboxylic acids with monoalcohols and polyalcohols, the liquid fatty phase consisting partially or totally of ester oil(s) having

a flash point equal to or greater than 40°C, to structure the said composition in the form of a transparent and/or translucent self-supporting solid with a hardness ranging from 20 to 2 000 gf and  
5 preferably from 20 to 900 gf and even better from 20 to 600 gf.

49. Use of a continuous liquid fatty phase comprising at least one ester oil chosen from the esters of monocarboxylic acids with monoalcohols and  
10 polyalcohols, essentially structured with a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- 15 - at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide,  
20 sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of  
25 25 to 250°C,

the liquid fatty phase consisting partially or totally of volatile oil(s) having a flash point equal

to or greater than 40°C, in a cosmetic composition or for the manufacture of a physiologically acceptable, transparent or translucent and/or transfer-free and/or non-sticky composition.

5           50. Use of a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group,  
10 consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane,  
15 thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

20           in a cosmetic composition or for the manufacture of a physiologically acceptable composition, containing a liquid continuous fatty phase comprising at least one ester oil chosen from the esters of monocarboxylic acids with monoalcohols and polyalcohols, to structure  
25 the said composition in the form of a transparent or translucent self-supporting solid.

51. Use of a continuous liquid fatty phase

comprising at least one ester oil chosen from the esters of monocarboxylic acids with monoalcohols and polyalcohols, essentially structured with a sufficient quantity of at least one polymer (homopolymer or 5 copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in a 10 chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, 15 and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or 20 totally of volatile oil(s) having a flash point equal to or greater than 40°C, in a transparent or translucent cosmetic composition or for the manufacture of a physiologically acceptable transparent or translucent composition, as agent for improving the 25 non-transfer of the composition and/or reducing the stickiness of the composition.

52. Use of at least one ester oil chosen

from esters of monocarboxylic acids with monoalcohols and polyalcohols, in the continuous liquid fatty phase of a cosmetic composition or for the manufacture of a physiologically acceptable composition, one said fatty phase being essentially structured with a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one moiety comprising:

- 10 - at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing hydrogen interactions chosen from ester, amide, 15 sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and soluble in the liquid fatty phase at a temperature of 20 25 to 250°C, to confer properties of transparency and translucence of the said composition and/or a deposit of the said composition on keratinous materials.

53. Use according to any one of Claims 48 to 51, in which the composition has a hardness of 20 to 25 2 000 gf, preferably of 20 to 900 gf and even better of 20 to 600 gf.

54. Cosmetic method for reducing the



transfer and/or stickiness of a transparent or translucent cosmetic composition containing a liquid fatty phase comprising at least one ester oil chosen from the esters of monocarboxylic acids with  
5 monoalcohols and polyalcohols, consisting in structuring the said fatty phase with a sufficient quantity of at least one polymer (homopolymer or copolymer) having a weight-average molecular mass ranging from 500 to 500 000, containing at least one  
10 moiety comprising:

- at least one polyorganosiloxane group, consisting of 1 to 1 000 organosiloxane units in the chain of the moiety or in the form of a graft, and
- at least two groups capable of establishing  
15 hydrogen interactions chosen from ester, amide, sulphonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof,

the polymer being solid at room temperature and  
20 soluble in the liquid fatty phase at a temperature of 25 to 250°C,

the liquid fatty phase consisting partially or totally of ester oil(s).

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/15024

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 A61K7/02 A61K7/027 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 266 647 A (OREAL) 18 December 2002 (2002-12-18)  example 3	1-10, 12-36, 38-41, 43-45, 47-51,54
X	US 6 051 216 A (MOGHE BHALCHANDRA ET AL) 18 April 2000 (2000-04-18)  example 4	1-10, 13-36, 38-45, 47-51,54
A	US 5 874 069 A (CHEN HUIYONG PAUL ET AL) 23 February 1999 (1999-02-23) the whole document  --/--	1-54

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the International filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the International filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the International search

13 May 2004

Date of mailing of the International search report

04/06/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Yon, J-M

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/15024

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 594 285 A (GEN ELECTRIC) 27 April 1994 (1994-04-27) the whole document ----	1-54
A	US 2002/051758 A1 (URRUTIA-GUTIERREZ ADRIANA ET AL) 2 May 2002 (2002-05-02) page 8, paragraph 126 page 9, paragraph 128 page 9, paragraph 129 -----	1-54

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/15024

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1266647	A	18-12-2002	FR 2825915 A1	20-12-2002
			CN 1386490 A	25-12-2002
			EP 1266647 A1	18-12-2002
			JP 2002370919 A	24-12-2002
			US 2003072730 A1	17-04-2003
US 6051216	A	18-04-2000	AT 238371 T	15-05-2003
			AU 730357 B2	08-03-2001
			AU 8673698 A	22-02-1999
			BR 9811064 A	19-09-2000
			CA 2298703 A1	11-02-1999
			CN 1268151 T	27-09-2000
			DE 69813826 D1	28-05-2003
			DE 69813826 T2	01-04-2004
			EP 1000112 A1	17-05-2000
			ES 2198738 T3	01-02-2004
			HU 0002543 A2	28-12-2000
			JP 2001512164 T	21-08-2001
			NO 20000492 A	28-03-2000
			NZ 502604 A	01-02-2002
			PL 338438 A1	06-11-2000
			TR 200000438 T2	21-12-2000
			WO 9906473 A1	11-02-1999
			US 6353076 B1	05-03-2002
			ZA 9806823 A	31-01-2000
US 5874069	A	23-02-1999	AT 225644 T	15-10-2002
			AU 2601197 A	22-10-1997
			CA 2249325 A1	09-10-1997
			DE 69716250 D1	14-11-2002
			DE 69716250 T2	11-09-2003
			DK 891183 T3	10-02-2003
			EP 0891183 A1	20-01-1999
			ES 2185005 T3	16-04-2003
			PT 891183 T	28-02-2003
			WO 9736573 A1	09-10-1997
EP 0594285	A	27-04-1994	US 5272241 A	21-12-1993
			EP 0594285 A2	27-04-1994
			JP 2749762 B2	13-05-1998
			JP 6207019 A	26-07-1994
			US 5399653 A	21-03-1995
			US 5516869 A	14-05-1996
US 2002051758	A1	02-05-2002	AU 8853001 A	13-03-2002
			CA 2420518 A1	07-03-2002
			EP 1315474 A2	04-06-2003
			WO 0217870 A2	07-03-2002